Surface Engineering for Corrosion and Wear Resistance Application

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Lecture - 35
Corrosion Prevention

Hello, in this talk we will discuss about the different ways by which corrosion different types of corrosion can be prevented. So, if you talk about particularly in case of the aqueous corrosion, how should we take the important measures? So, that the corrosion kinetics can be reduced and it can be prevented to a large extent.

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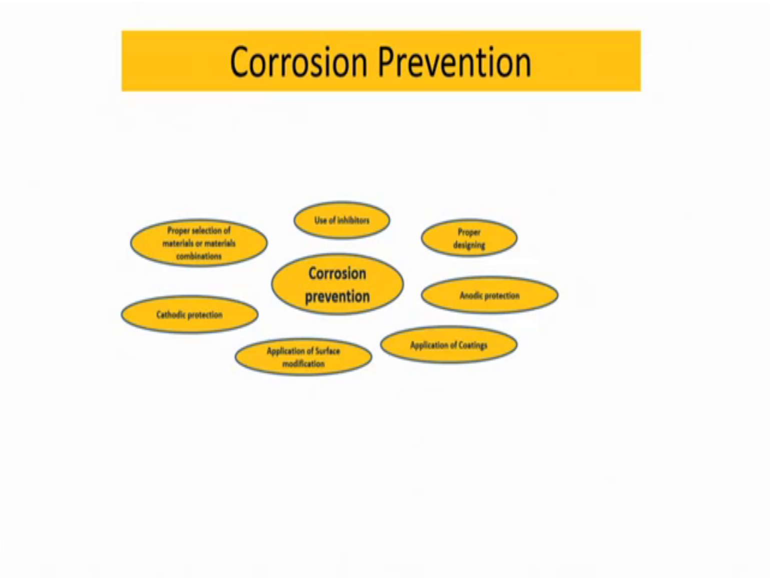

Corrosion Prevention

Corrosion prevention

Proper selection of materials or materials combinations

Use of inhibitors

Proper designing

Anodic protection

Cathodic protection

Application of Surface modification

Application of Coatings

So, this is the summary slide which shows the different ways by which corrosion may be prevented. Especially most of the ways that are applicable for combating the aqueous corrosion and some of the techniques are applicable for the combat combating the liquid metal corrosion some of the techniques are for high temperature oxidation.

So, if you talk about the aqueous corrosion, it is basically it these are basically aqueous corrosion based problem can be circumvented or maybe can be reduced by a choice of the proper materials by the application of cathodic protected cathodic protection by the application of anodic protection, by the application of the inhibitors where you change the environment by proper designing of the component and by application of surface modification and coating techniques.

Now if you talk about high temperature oxidation ways corrosion high temperature oxidation ways corrosion can be avoided or can be minimized by proper choice of material. In that specific environment it can be minimized by application of surface modification particularly surface alloying, it can also be minimized by the application of coating.

Now, if you talk about liquid metal corrosion and liquid metal corrosion can be avoided by proper selection of the materials combination, you can also get rid of the liquid metal base corrosion by the application of coating. So, you have to understand that which kind of corrosion your component is facing in that particular environment. So, accordingly you choose the material and just go on taking different precautionary measures, so that corrosion can be minimized.

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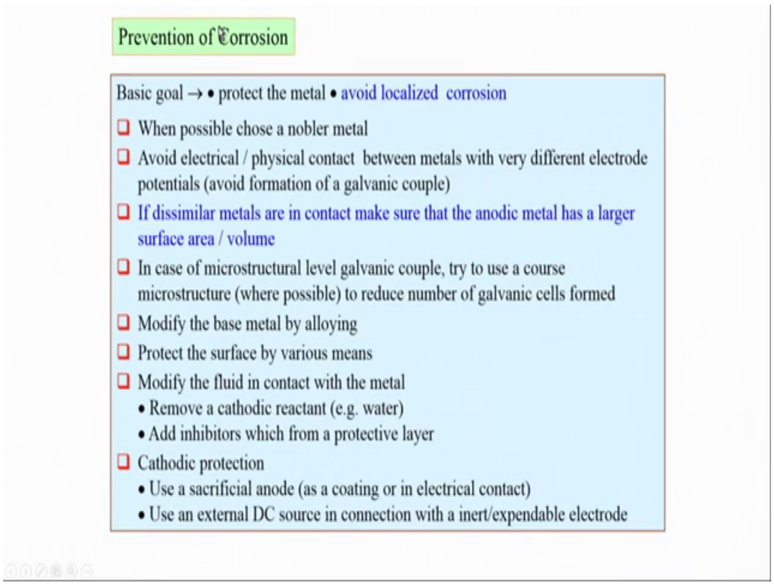

Prevention of Corrosion

Basic goal → • protect the metal • avoid localized corrosion

❑ When possible chose a nobler metal
❑ Avoid electrical / physical contact between metals with very different electrode potentials (avoid formation of a galvanic couple)
❑ If dissimilar metals are in contact make sure that the anodic metal has a larger surface area / volume
❑ In case of microstructural level galvanic couple, try to use a course microstructure (where possible) to reduce number of galvanic cells formed
❑ Modify the base metal by alloying
❑ Protect the surface by various means
❑ Modify the fluid in contact with the metal
  - Remove a cathodic reactant (e.g. water)
  - Add inhibitors which from a protective layer
❑ Cathodic protection
  - Use a sacrificial anode (as a coating or in electrical contact)
  - Use an external DC source in connection with a inert/expendable electrode

So, now this is the summary sheet our basic goal is to protect the material from corrosion and avoid the localized corrosion. So, whenever is possible you choose that is a typical thumb rule thumb rules which must be followed for minimizing the corrosion kinetics in actual component. Like whenever is possibly choose the nobler materials like the material nobler or otherwise in that material some stable film form specific film forms which protects underlying substrate.

Then avoid electrical or physical contact between the metals to avoid the to get rid of the problem of the galvanic corrosion if dissimilar metals are in contact make sure that the anodic metal has a larger area to volume ratio that is typical design. Criteria you have to follow the proper thumb rule for designing of the component, component dissimilar components particularly. In case of micro structure level galvanic couple try to use a coarse microstructure to reduce number of galvanic cells course microstructure or in other word, I must say try to use the homogeneous component with homogeneous microstructure.

So, that there is no chance or for possibility of formation of micro galvanic cell even if it is form, it is basically uniform all throughout. Modify the base alloy by alloying, then protect the surface by various means like painting or use some alloying operation or use some coating. So, modify the fluid by the application of different inhibitors and cathodic protection or anodic protection. Cathodic protection use a sacrificial anode or may be a external dc source in connection with the inert or expended cable. So, these are the different precautionary measures you must take in order to get rid of the aqueous corrosion problem.

If you talk about the high temperature oxidation problem as I mentioned you then you have to apply certain alloying element on the surface by the process of surface alloying, either by pack cementation base surface alloying process or by the application of laser surface alloying. So, that whatever surface you are modifying that is basically protective in that particular environment. Protective in that environment means that, whatever film is formed out of that alloying element that film is highly stable in terms of it is strength in terms of it is diffusivity through the, these to that oxide is very low, in terms of ionic conductivity. So, these same which are forming on the surface is highly protective in nature.

Whenever it is the case for liquid metal corrosion, then in that case you basically you can apply that coating which can either use change the material or use proper material in that proper liquid corrosion environment liquid metal environment or apply a very thin layer of coating which is actually you does which does not protect the which does not participate in the liquid metal and (Refer Time: 05:32) process, and by that process it modifies the underlying substrate. It basically protects the underlying substrate.

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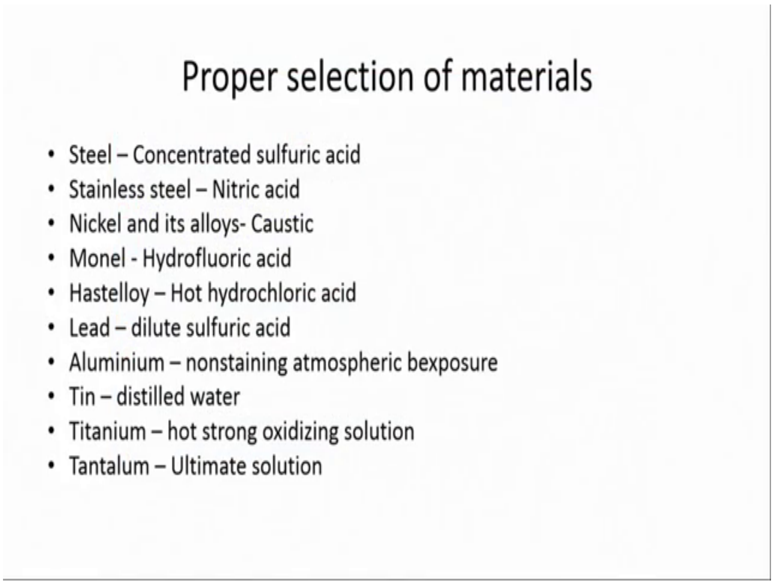

Proper selection of materials

- Steel – Concentrated sulfuric acid
- Stainless steel – Nitric acid
- Nickel and its alloys- Caustic
- Monel - Hydrofluoric acid
- Hastelloy – Hot hydrochloric acid
- Lead – dilute sulfuric acid
- Aluminium – nonstaining atmospheric bexposure
- Tin – distilled water
- Titanium – hot strong oxidizing solution
- Tantalum – Ultimate solution

So, these are the guidelines which you must follow for preventing or for minimizing the probability of different types of corrosion. Now if you talk about proper selection of materials especially the aqueous corrosion base problem, you will find that different materials you behave differently. And these charts gives you guidelines about which material which behave or which material will not corroded in particular environment particularly when this is the case for general corrosion. Because for stress corrosion cracking we saw separate least for liquid metal embrittlement we saw separate list.

So, particularly for general corrosion base problem steel is highly safe to carry concentrated sulfuric acid. Stainless steel is highly safe to carry the nitric acid in the a nitric acid solution. Nickel and it is alloys very safe in caustic solution, Monel is very safe in hydrochloric acid solution. Hastelloy is safe in hot hydrochloric acid lead is safe in dilute sulfuric acid. Aluminium is safe in nonstaining atmospheric exposure, tin is safe in distilled water. Titanium is safe in hot strong oxidizing solution; tantalum is safe in all environments.

So, this gives you a proper guideline of the choice of material particularly the corrosion particularly for that case corrosion is basically general corrosion based problem. But if it is stress corrosion base problem, then you have to follow the chart for the stress corrosion. If it is liquid metal embrittlement you have to follow the chart for liquid metal embrittlement. Whenever it is high temperature oxidation, you have to follow (Refer

Time: 07:24) diagram or also you have to follow the typical alloy or you have to choose the different alloy which actually does not undergo corrosion in that particular environment by forming a very thin protective oxide film.

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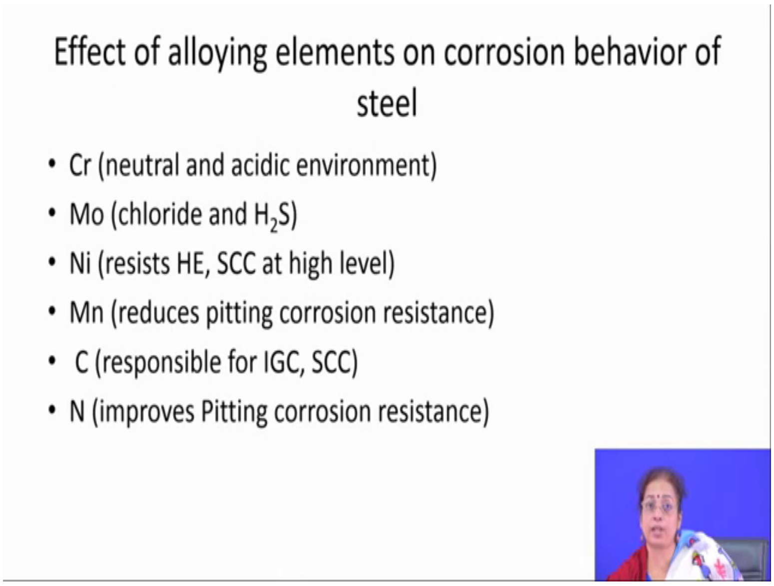

Effect of alloying elements on corrosion behavior of steel

- Cr (neutral and acidic environment)
- Mo (chloride and H_2S)
- Ni (resists HE, SCC at high level)
- Mn (reduces pitting corrosion resistance)
- C (responsible for IGC, SCC)
- N (improves Pitting corrosion resistance)

So, proper choice of (Refer Time: 07:43) material is very important. Usually sometimes you do alloying also to reduce the corrosion tendency like; chromium is alloyed usually because chromium saves the material from neutral and acidic environment. Molybdenum saves in chloride and sulfuric acid environment, nickel resistor stays corrosion cracking at higher level, manganese reduces the pitting corrosion resistance, molybdenum reduces a pitting corrosion. Molybdenum manganese reduces a pitting corrosion resistance, molybdenum enhances a pitting corrosion resistance property carbon is responsible for inter granular corrosion stays corrosion cracking.

So, nitrogen improves that we show these are the few guidelines where the role of alloying element in controlling their different proper different corrosion behavior or corrosion property must be due to you prior to designing the alloy for specific application.

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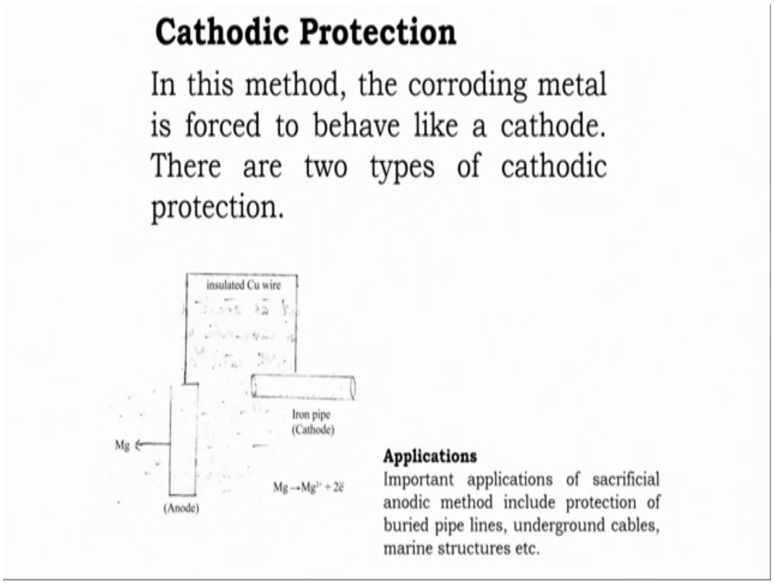

Cathodic Protection

In this method, the corroding metal is forced to behave like a cathode. There are two types of cathodic protection.

Applications

Important applications of sacrificial anodic method include protection of buried pipe lines, underground cables, marine structures etc.

Now, second technique which I will discuss is that Cathodic Protection system; which is mostly applied or can be applied widely for protection of the surface against the aqueous corrosion base problem. So, cathodic protection is nothing, but a kind of technique why do you make the component of your choice as cathode. So, this can be done by two ways first way is by just attaching it by or may connecting it with another material which is anodic to that metal to a large extent. So, when you connect an anode with this here with your component then what happens is that corrosion is that corrosion process is surrounding by the is surrounded by the or corrosion basically proceeds in the anode.

Anode is mainly subjected to the corrosion. So, whenever the anode is subjected to corrosion, naturally by corrosion there is evolution a lot of electron and that electron whenever is evolved naturally your cathode is highly protected; through your metal is highly protected otherwise also it is acting as cathode so, there is no corrosion at all.

So, this is very important way of protecting the metal from any kind of corrosion say maybe any kind of aqueous corrosion I must say it may be general corrosion, it may be it may be pitting corrosion, it may be stress corrosion cracking, it may be hydrogen embrittlement.

So, any kind of corrosion can be taken care of by typical cathodic protection process by this cathodic protection you basically make your component as cathode and by this process naturally indirectly you minimize the corrosion you cannot get rid of the problem of the corrosion to a large extend.

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Cathodic protection

So, this is the typical cathodic protection which is observed in pipeline for example, whenever it is not protected you see lot of rust on the component, but whenever it is protected by difficult exposing by connecting it to typical anode anodes you will find that this is highly last year a surface and it is protected. So, this is basically a kind of galvanized steel. So, galvanized steel whenever you use naturally it protects the surface by 2 ways; one way is by typical, one way is by typical barrier coating another way is by sacrificial coating where it flat protects the underlying substrate by cathodic protection.

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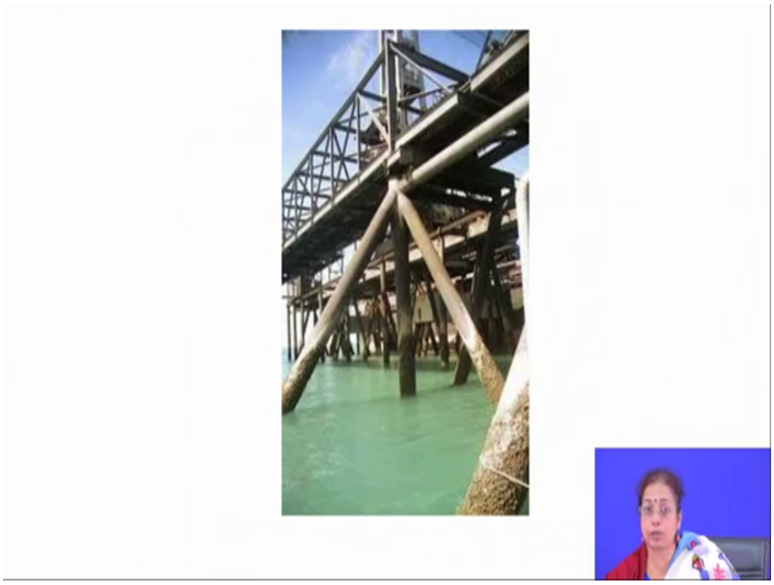

Similarly, this is the case for bridge, bridges you are usually connected to magnesium magnesium pieces like; anodes at regular interval by typical wire. So, whenever the magnesium magnesium anodes are there all throughout the bridges at regular interval what happens is that, corrosion happens in magnesium in contrast to that of your steel. So, your steel structure is protected.

So, what you have to do is that at regular interval you have to inspect the corrosion rate of the corroded species corroded magnesium. So, that you can say that whether corrosion whether your steel can be protected further. And or otherwise you can also you can also estimate the amount of the or volume of the magnesium required for protecting the component for several years or accordingly you can also calculate the lifetime of the component. So, this particular means is a very widely used weeds are protecting the large structure against the corrosion process.

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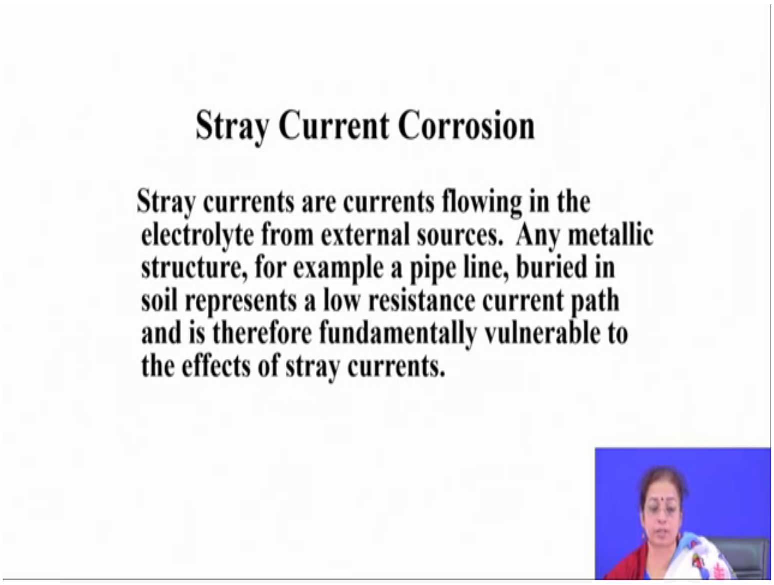

Stray Current Corrosion

Stray currents are currents flowing in the electrolyte from external sources. Any metallic structure, for example a pipe line, buried in soil represents a low resistance current path and is therefore fundamentally vulnerable to the effects of stray currents.

But one of the important problem associated with that cathodic protection is a Stray Currents which happens in the electrolyte from external sources. So, whenever you use cathodic protection particularly below that of earth there you will find that because of the cathodic protection protected or because of cathodic protection especially when you just do connect it with dc sources you will find that if there is any other corroded species they gets corrodes away. So, that gets further trouble. So, you have to be pretty much careful in building the structure next to the cathodically protected structure. So, that it cannot corrode.

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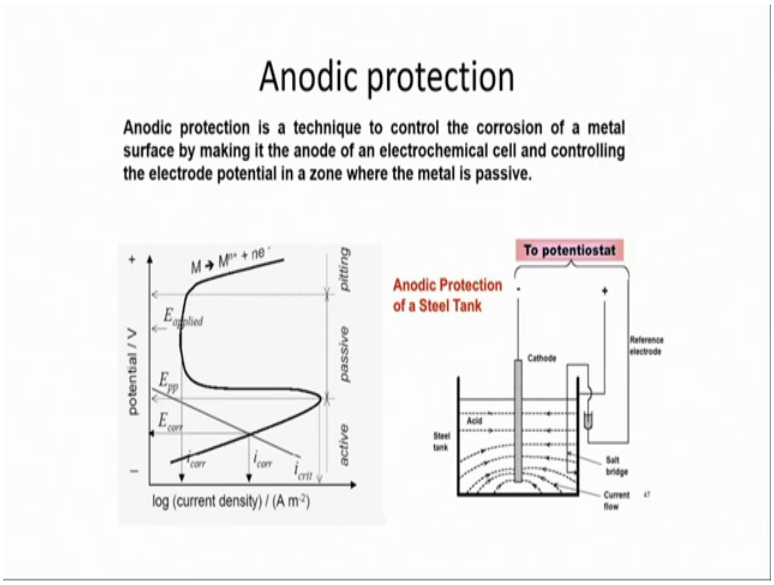

Anodic protection

Anodic protection is a technique to control the corrosion of a metal surface by making it the anode of an electrochemical cell and controlling the electrode potential in a zone where the metal is passive.

Through another way of protecting the surface by is by Anodic protection. This is completely the reverse case instead of connecting the surface with more anodic material or maybe passing the electrical current. So, that your components act as canoed you cathode you use the reverse way that is you try to use your component as anode by basically connecting it with the electrical sources power sources. So, when it is acting as anode naturally you will see that the corrosion rate of your component increases to a large extent.

So, when it increases to a large extent naturally there is a formation of the oxide scale on the surface. So, when there is formation of oxide scale on the surface you will find that they are passivated they say the you say it has passivated and that passive film actually helps in reducing the corrosion rate further. So, this is the case for the self passivation by the anodic current.

So, you will find that the component gets protected. So, this particular anodic protection is applied only for those particular component which is very prone to corrode actually. And where there is formation of passive film and that passive film is highly protective in nature.

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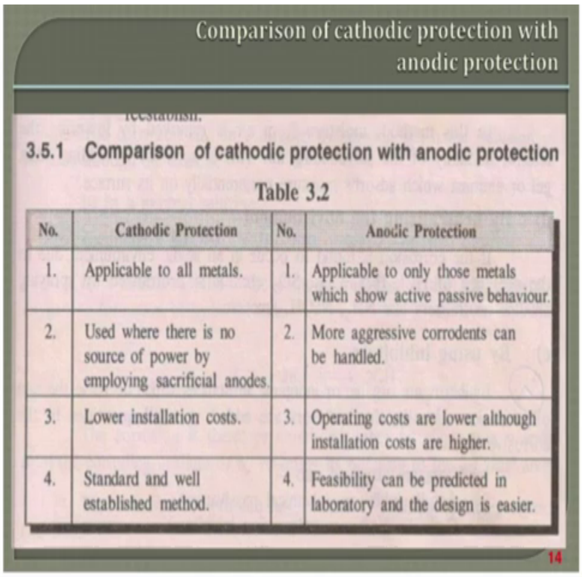

Comparison of cathodic protection with anodic protection

3.5.1 Comparison of cathodic protection with anodic protection

Table 3.2

No.	Cathodic Protection	No.	Anodic Protection
1.	Applicable to all metals.	1.	Applicable to only those metals which show active passive behaviour.
2.	Used where there is no source of power by employing sacrificial anodes.	2.	More aggressive corrodents can be handled.
3.	Lower installation costs.	3.	Operating costs are lower although installation costs are higher.
4.	Standard and well established method.	4.	Feasibility can be predicted in laboratory and the design is easier.

So, if you compare the cathodic protection and that of a anodic protection you will can you can understand that, cathodic protection is more versatile can be applied for any materials and can be applied for getting rid of any kind of aqueous corrosion problem.

But anodic protection system anodic protection can only be applied which under goes active passive transformation at a active passive behaviour.

And more aggressive part corrodents can be handled. So, operating cost of cathodic and anodic you will find that operating cost are lower in anodic protection; although installation cost is higher and cathodic protection is having always lower cost lower cost. And cathodic protection is a standard system and well established and feasibility can be I do not actually anodic protection you have to know actually whether at all anodic protection can be applied for this material.

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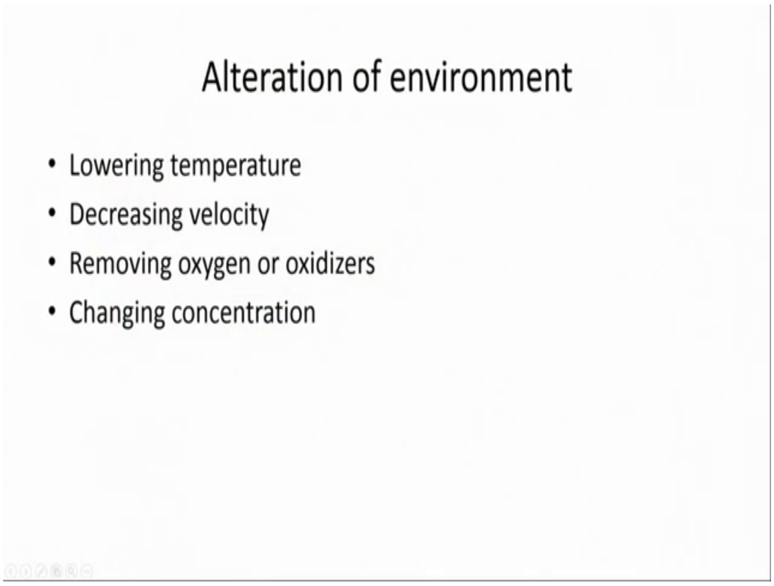

Alteration of environment

- Lowering temperature
- Decreasing velocity
- Removing oxygen or oxidizers
- Changing concentration

So, you can say that cathodic protection is highly versatile and can be widely use for all kind of materials. You can also change the environment so, if you talk about changing the environment can be done by just by getting rid of the external parameter. So, reducing the external parameters, which aggravates the corrosion rate like; velocity aggravates the corrosion rate. So, if you decrease the velocity or corrosion rate will be reduced, if you reduce the temperature corrosion rate will be reduced.

Because even though corrosion is happens in aqueous media, but kinetics it is against thermally activated process. So, as you go on increasing temperature rate of corrosion increases. You can also remove oxygen or oxidizer you can also change the concentration. So, by these all ways you can always alter the environment.

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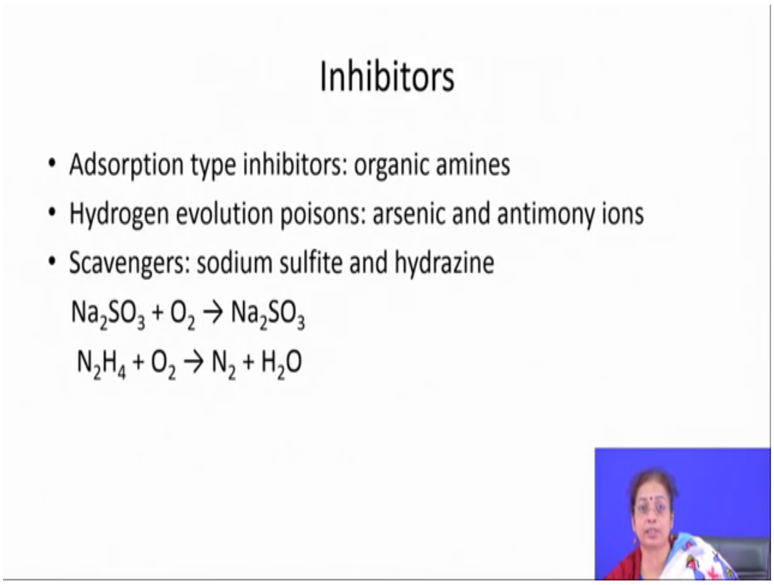

Inhibitors

- Adsorption type inhibitors: organic amines
- Hydrogen evolution poisons: arsenic and antimony ions
- Scavengers: sodium sulfite and hydrazine

$Na_2SO_3 + O_2 \rightarrow Na_2SO_3$

$N_2H_4 + O_2 \rightarrow N_2 + H_2O$

So, if you talk about altering the environment as I mentioned you can reduce the temperature you can reduce the velocity, but sometimes these are not under your hand. So, you cannot really play with them because those are the natural things and where you have to use your component. So, in that case you can apply inhibitors to reduce the aggressiveness of the media aggressiveness of the particular environment.

So, if you talk about inhibitors there again added when added in the solution or in the environment; the either reduces the aggressiveness of the environment or it take away some species who is called cause corrosion or other way otherwise it can also get absorbed over the surface and by that process protects the surface. So, there are different types of inhibitors available, which are applied to protect the surface from corrosion purpose they are adsorption type inhibitors hydrogen evolution poisons and these scavengers.

So, adsorption type inhibitors means oxide that it basically get absorbed over the surface like organic mind. So, you just sprinkle it in the environment it gets adsorbed over the surface and by that process, it acts as a barrier the surface is no more in contact with the solution. When it is hydrogen evolution poisons like; I arsenic and antimony ions in basically takes away it basically it is poisonous basically which can reduces the tendency of hydrogen evolution. And by that process it reduces the tendency of those corrosion particularly hydrogen embrittlement, stress corrosion cracking problem to a large extent.

Scavengers again takes away oxygen from the system like sodium sulfide and hydrogen they basically takes away oxygen from the system and by that process, it reduces the aggressiveness of the environment.

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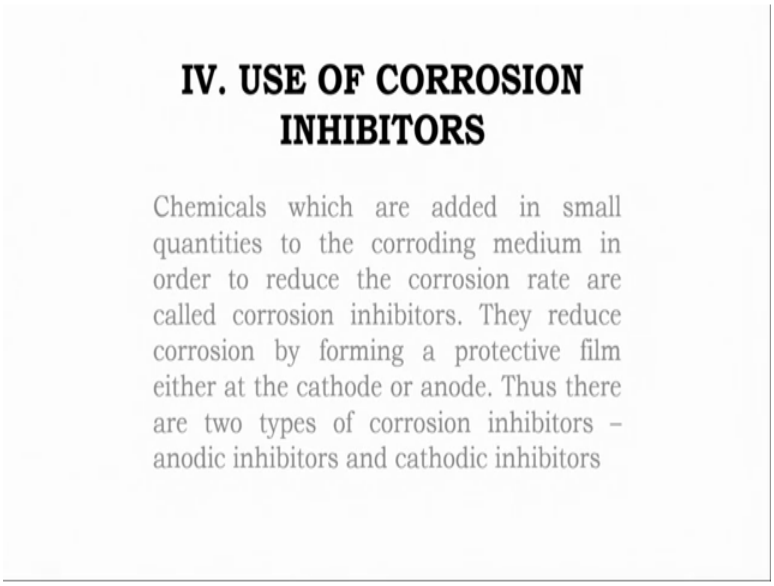

IV. USE OF CORROSION INHIBITORS

Chemicals which are added in small quantities to the corroding medium in order to reduce the corrosion rate are called corrosion inhibitors. They reduce corrosion by forming a protective film either at the cathode or anode. Thus there are two types of corrosion inhibitors – anodic inhibitors and cathodic inhibitors

So, Corrosion Inhibitors is very important. So, it is nothing, but chemicals which are added in small quantities to the corroding media. In order to reduce the corrosion rate they reduce the corrosion by forming a protective film either at the cathode or anode, they are there are two types of inhibitors like; cathodic inhibitor or anodic inhibitors or also mixed inhibitors.

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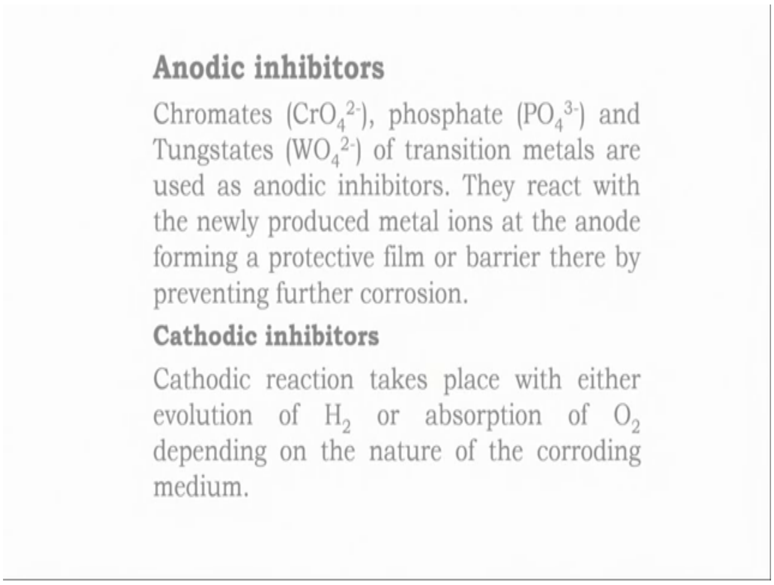

Anodic inhibitors

Chromates (CrO_4^{2-}), phosphate (PO_4^{3-}) and Tungstates (WO_4^{2-}) of transition metals are used as anodic inhibitors. They react with the newly produced metal ions at the anode forming a protective film or barrier there by preventing further corrosion.

Cathodic inhibitors

Cathodic reaction takes place with either evolution of H_2 or absorption of O_2 depending on the nature of the corroding medium.

So, anodic inhibitors actually they are basically like a chromate, phosphate the tungstates. Their anodic inhibitors they react with the metal surface and then form protective film of barrier that are preventing further preventing further corrosion.

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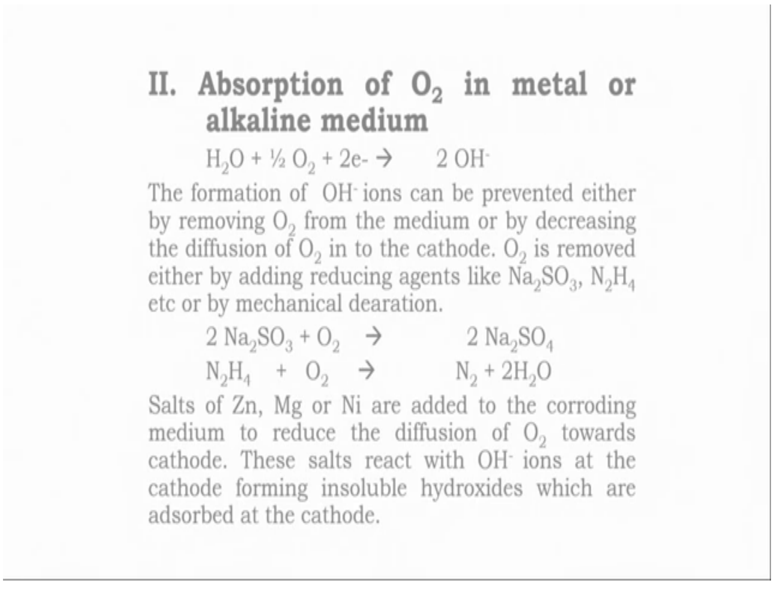

II. Absorption of O_2 in metal or alkaline medium

$$H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2 OH^-$$

The formation of OH^- ions can be prevented either by removing O_2 from the medium or by decreasing the diffusion of O_2 in to the cathode. O_2 is removed either by adding reducing agents like Na_2SO_3, N_2H_4 etc or by mechanical dearation.

$$2 Na_2SO_3 + O_2 \rightarrow 2 Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

Salts of Zn, Mg or Ni are added to the corroding medium to reduce the diffusion of O_2 towards cathode. These salts react with OH^- ions at the cathode forming insoluble hydroxides which are adsorbed at the cathode.

So, anodic inhibitors are very interesting they basically helps in the process of formation of thin protective film as you see in case of that typical anodic process of the anodic protection system. So, do you means more or less similar in case of anodic protection you basically allow the component to act as anode. So, that there is formation of a thin continuous passive film.

So, anodic inhibitors also you add in that system in such a fashion that they react with the metal surface and form the metal compound. So, that it is preventing further corrosion and cathodic react cathodic inhibitors at the inhibitors they are basically; they their reaction takes place with either evolution of a hydrogen or absorption of oxygen depending on the nature of the corroding media. So, they make your component basically cathode. So, that does not react with any mode because whatever hydrogen or whatever oxygen your general thing they get consumed by the inhibitors.

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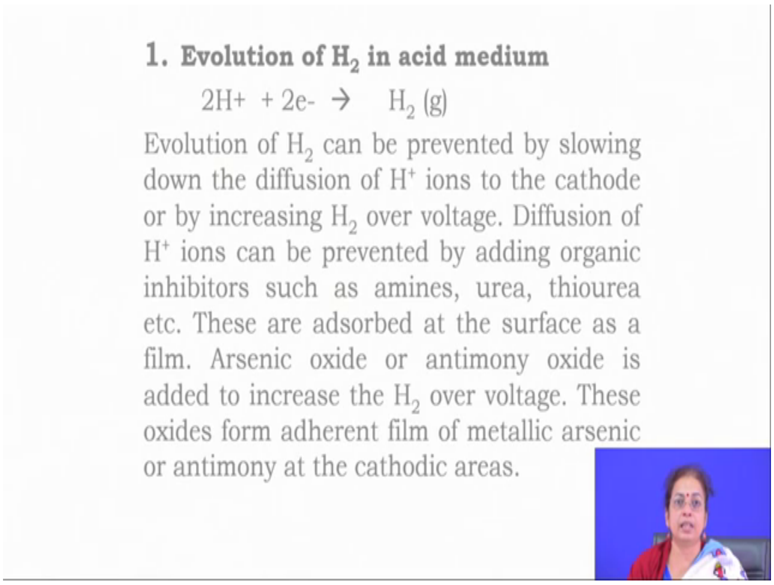

1. Evolution of H_2 in acid medium

$2H^+ + 2e^- \rightarrow H_2 (g)$

Evolution of H_2 can be prevented by slowing down the diffusion of H^+ ions to the cathode or by increasing H_2 over voltage. Diffusion of H^+ ions can be prevented by adding organic inhibitors such as amines, urea, thiourea etc. These are adsorbed at the surface as a film. Arsenic oxide or antimony oxide is added to increase the H_2 over voltage. These oxides form adherent film of metallic arsenic or antimony at the cathodic areas.

So, there is always hydrogen evolved with the media. So, evolution of hydrogen can be prevented by slowing down the diffusion of hydrogen ion to the cathode or by decreasing the hydrogen over voltage. Defuse of hydrogen ion can be prevented by adding organic inhibitors such as amines, urea, thiourea they are absorbed at the surface as film. Arsenic oxide or antimony oxide is added to replace the hydrogen over voltage; these oxides form a adherent film of metal arsenic or antimony at the cathodic sites.

So, so absorption of oxygen can be done by typical sodium sulfate, so hydrazine these kind of agents are chemical compound they basically consumes hydrogen consumes oxygen from the system. So, when they are consume oxygen from the system, so no more free oxygen is available as a result of which your component get protected.

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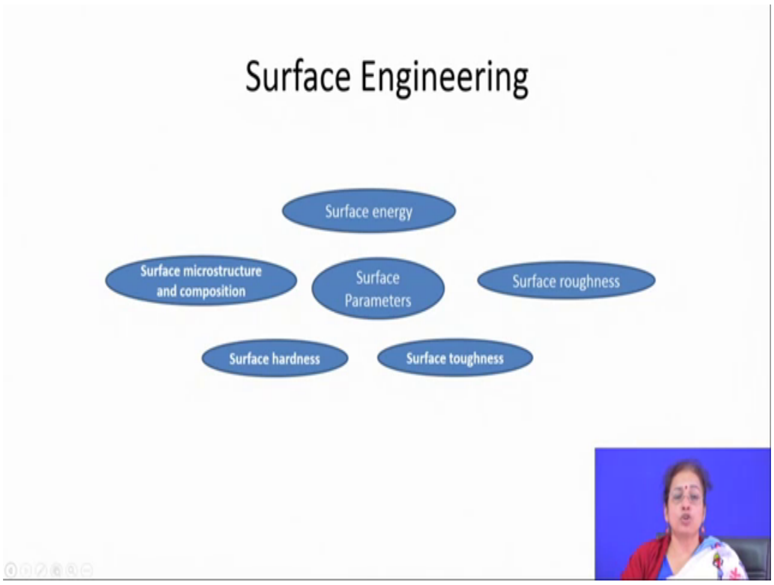

Surface Engineering

So, finally, the corrosion can be prevented by the application of surface engineering techniques. So, if you think about different surface engineering techniques that or maybe different surface parameters, which control the corrosion kinetics they may be categorized into different different sectors like; first important parameter which controls the corrosion kinetics is surface energy. So, if you just having if you just expose the surface with higher energy, it will be more prone to corrosion on the other hand if you expose the surface with lower energy; it will be less prone to corrosion.

Surface roughness space very important role rougher the surface more will be the exposed surface area, as a result of which more corrosion will be there. Particularly when surface is very rough you will find that there will be chance of more pit formation also, at the surface rough region because they may act as a site for PTD session. They make act as site for the stress corrosion cracking initiation. So, surface roughness plays a very important role in controlling the meaning of the initiation, we kind of in addition to increasing the overall surface area of the component.

Microstructure and composition they are very important because ultimately it is a surface microstructure and composition which controls everything. So, if it is uniform microstructure and composition; then it will the corrosion made will be mode will be uniform. If it is non uniform there we be galvanic corrosion there if it is around wave boundary several precipitates then there will be inter granular corrosion there may be some stress corrosion cracking problem. So, surface micro structure and composition is very important which controls everything.

Surface hardness is also important because, surface hardness influences the erosion corrosion behaviour it can also influence the stress corrosion behaviour to a large extent. And finally, fracture toughness; fracture toughness is another parameter which controls many corrosion problem like stress corrosion cracking problem is controlled by surface roughness.

Surface roughness then again if you talk about cavitation corrosion, cavitation corrosion is controlled by surface roughness. So, these are the parameters which control the aqueous corrosion property of the component. If you talk about high temperature oxidation then high temperature oxidation is predominantly controlled by surface energy then surface micro structure and composition and surface roughness.

If you talk about liquid metal corrosion it is controlled by surface micro structure and composition and then surface roughness. So, like that you have to know what are the parameters which control the differents different corrosion properties and also you have to know the, what exact values you are looking for. For improving the corrosion resistant to this particular level what micro structure and composition I am looking for. So, like that you have to design the surface very nicely when in advanced. So, that you get the desired property, then you can go on modifying further by different other nodes.

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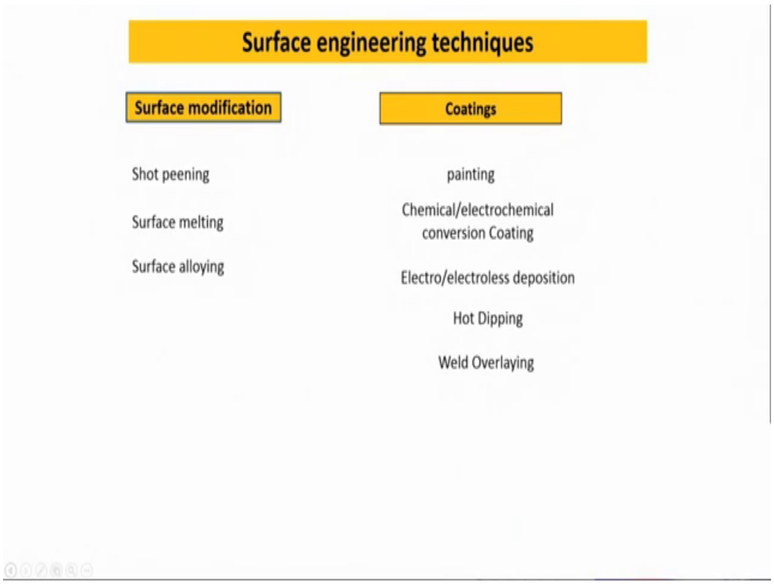

Surface engineering techniques

Surface modification

- Shot peening
- Surface melting
- Surface alloying

Coatings

- painting
- Chemical/electrochemical conversion Coating
- Electro/electroless deposition
- Hot Dipping
- Weld Overlaying

Now, coming to the different techniques which are available for the corrosion protection they may be categorized under 2 types; one is surface modification and coating second one is coating. So, surface engineering techniques and I think about tools which are applied to change the surface or to tailor the surface. So, they maybe categorize into 2 types on a surface modification another one is surface coating.

Surface modification deals with a series of technique where you modify the existing surface. So, that it is part of the surface part of the component on the other hand coating deals with a series of technique where you apply completely another layer on the surface. So, there is a sharp interface or diffused interface between the coated layer and the component. So, if you talk about different surface modification techniques may be applied for mitigation of the corrosion they are of 3 types one is shot peening surface, second one is surface melting, third one is surface alloying.

So, shot peening can be applied for introduction of the stress on the in the component. So, shot peening is a very important categories of surface modification technique and usually it can also be applied for modification of the surface in case of stress corrosion cracking, in case of corrosion fatigue, it can also be applied for mitigation of the corrosion. Especially when the pitting corrosion is there so, these all kind of corrosion where stress is responsible there the shot peening can be applied.

Similarly, another type of surface modification technique is surface melting. So, surface melting especially can be applied for homogenization of the microstructure. Specially when you built with the help of high energy laser or electron beam. So, when you go on melting the surface using high energy laser or electron beam it basically defines an homogenization microstructure. So, by that process it can control some of the corrosion problem like inter granular corrosion, it can control the galvanic corrosion, it can also control the stress corrosion cracking to a little extent.

Finally, surface alloying is another surface modification technique which basically enriches the surface with other alloying element and which prevents the corrosion to a large extent. So, surface alloying may be applied for prevention of the corrosion particularly when it is when it is of for example, galvanic corrosion when if it is of a high temperature oxidation if it is of a general corrosion surface alloying may be applied. So, these are the 3 surface modification techniques which might be applied to convert the corrosion problem.

If you talk about coating techniques which may be applied they are painting first of all painting is a versatile technique which is widely applied for protection against corrosion of any kind of material when exposed to the environment. It acts as a barrier layer and saves the surface from corrosion.

Chemical electrochemical conversion coatings can be applied for protection against corrosion, electro electroless deposition can be applied, hot dipping can be applied for protection against oxidation because hot dipping basically applies a very thin layer of can be a used for application of zinc coating or aluminium coating. So, by that process it saves the surface from oxidation.

Weld overlaying is another technique which can be applied for development of a thick hard coating; it may be called as hard facing. So, weld overlaying maybe applied for medication of the corrosion like cavitation corrosion for the mitigation of pitting corrosion these all corrosion can be mitigated by the process of weld overlaying.

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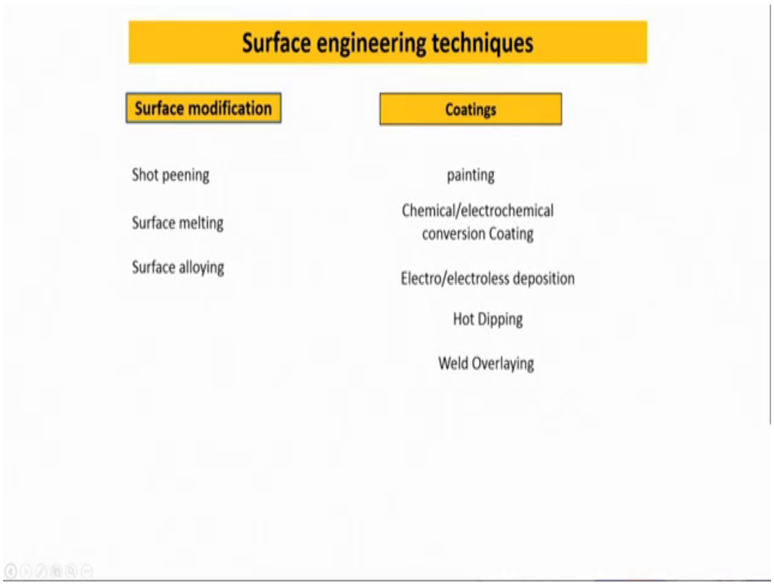

Surface engineering techniques

Surface modification

Shot peening

Surface melting

Surface alloying

Coatings

painting

Chemical/electrochemical conversion Coating

Electro/electroless deposition

Hot Dipping

Weld Overlaying

So, these are the different techniques which are applied and then we will be discussing about these few techniques in the next classes and have already been discussed some of the techniques so.

Thank you very much.