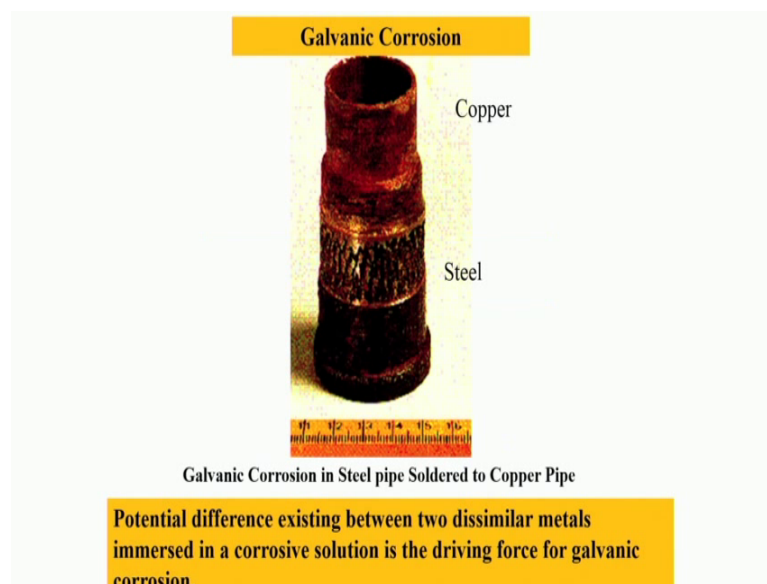


Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 13
Corrosion – II

Hello, so in this lecture I will discuss about the second mode of Corrosion that is aqueous corrosion particularly, that is galvanic corrosion.

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So, galvanic corrosion is a form of corrosion which usually occurs when two dissimilar metallic materials are electrically connected and they are placed in an aqueous media or electrolyte. So, usually the potential difference existing between the two dissimilar materials is a driving force for the corrosion to occur.

So, this is the case for copper and steel which is actually soldered. So, we will see that there is extensive corrosion at the steel surface of this particular steel part of the pipe pipeline combinations as compared to that of copper. This is because of the fact that steel is basically, more prone to prone to corrosion or active as compared to that of copper.

So, when two materials are actually joined together you would see that the steel basically goes on corroding as and as there is a so of electron or evolution of electron, that electron actually saves the copper to a large extend. So, like that you will find that

steel goes on corroding and that corrosion proceeds from the junction point towards the other end of the particular pipeline.

So, these galvanic corrosion can be a dangerous form of corrosion which basically starts at the interface and then proceeds to a large extent towards the other side of the component. And it is naturally a kind of localized form of corrosion and when it occurs in many cases not only in dissimilar combinations, but when the metal which is having dissimilar phases there also depending on the that corrosion probability or EMF of the individual phases. You will find that corrosion there may be a micro galvanic cell formation and as a result of which galvanic corrosion proceeds.

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Metals and alloys are arranged in a qualitative scale which gives a measure of the tendency to corrode → *The Galvanic Series*

Galvanic series

Galvanic series in marine water

<i>Noble end</i>	<i>More reactive</i> →									<i>Active end</i>
18-8 SS <i>Passive</i>	Ni	Cu	Sn	Brass	18-8 SS <i>Active</i>	MS	Al	Zn	Mg	

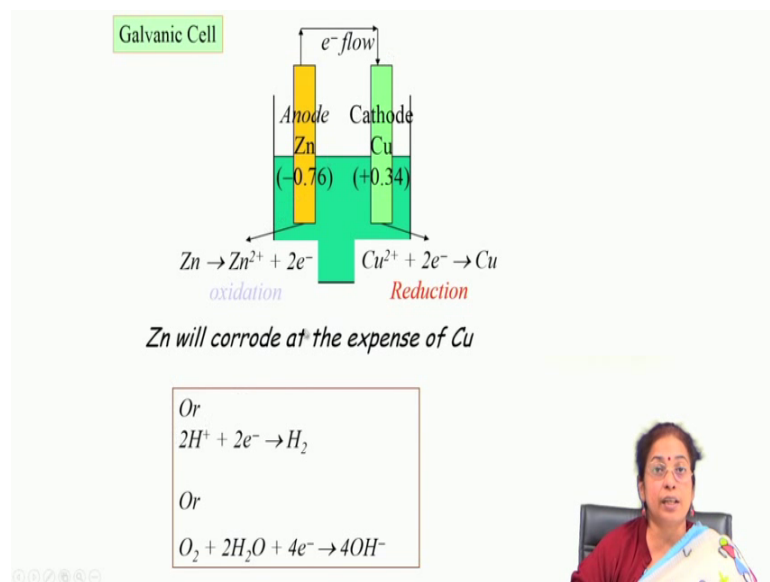
So, usually metals and alloys if you just talk about general corrosion or atmospheric corrosion in normal environment they are basically standard EMF series plays very important role to choose the materials. But whenever you talk about the application of metals and alloys in quantitative application of metals and alloys in normal environment actual environment, there the series which is applied is galvanic series.

So, that galvanic series is nothing, but it gives you information about the relative corrosion, potential of that different metals in that different in the metals as well as alloys in different environment and that galvanic series plays a very important role to choose the materials for galvanic combination. So, basically you have to be careful to choose the

materials for that to prevent the galvanic corrosion you have must choose the materials which are very close in the galvanic series for the prevention of galvanic corrosion.

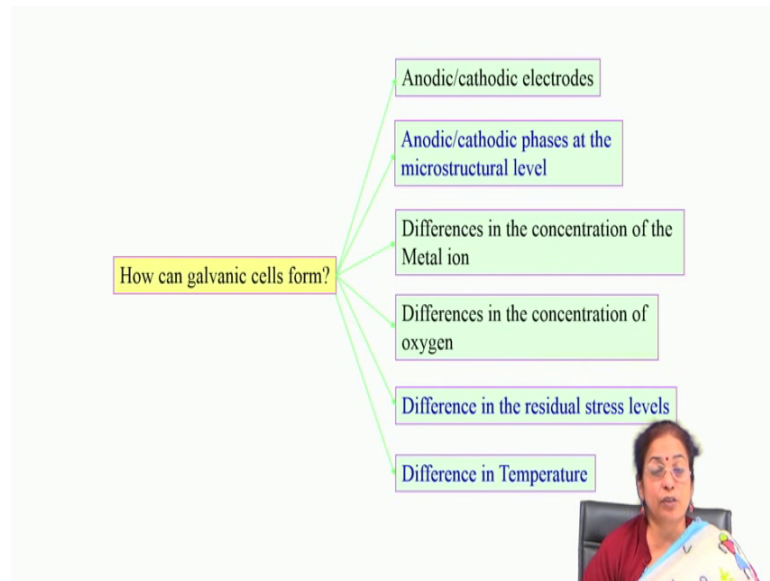
So, this is typical example of the galvanic series were like different steels as well 18 8 SS steel, which is passive and noble naturally and then nickel and then copper tin brass, 18 8 again it is ms aluminum, zinc, magnesium they are actually they are sequentially arranged from the noble end to the active end in marine water environment. So, as I mentioned you that the driving force for this galvanic corrosion is the potential difference the EMF difference of the two metal when they are joint together in aqueous environment.

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So, this is the case for the zinc and copper whenever you immerse it in typical hydrochloric acid solution you will find that and if you have connect them properly you will find that the zinc corrodes and at the expense of copper. So, copper is actually protected, but zinc goes on corroding to a large extent. So, this is typical galvanic cell.

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And you will find that the galvanic cell formation usually occurs or galvanic corrosion usually is observed not only when you just connect two dissimilar materials or two dissimilar metal together, but also it can occur by different other reasons as well. For example, if any as I mentioned you in any microstructure if you have different phases and different phases having different corrosion potential you will find that, they will be micro galvanic micro galvanic cell formation between two different phases.

And as a result of which problem starts at the interface and it proceeds thereafter. When there is difference in concentration of the metallic ion, then also the galvanic cell might form, difference in concentration of the oxygen there also there may be galvanic cell formation, difference in residual stress level.

So, for example, in one case the you just partially cold work on metal and other part is actually crystallized or annealed you will find that due to residual stress difference the cold works side is corroded to a large extent as compared to that annealed side. Similarly, difference in temperature if there is difference in temperature usually high temperature regime acts as a anode; anode as compared to that of low temperature regime.

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- ❑ Different phases (even of the same metal) can form a galvanic couple at the microstructural level (*In steel Cementite is noble as compared to Ferrite*)
- ❑ Galvanic cell may be set up due to concentration differences of the metal ion in the electrolyte → *A concentration cell*
 - Metal ion deficient → anodic
 - Metal ion excess → cathodic
- ❑ A concentration cell can form due to differences in oxygen concentration
 - Oxygen deficient region → anodic
 - Oxygen rich region → cathodic
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
- ❑ A galvanic cell can form due to different residual stresses in the same metal
 - Stressed region more active → anodic
 - Stress free region → cathodic
- ❑ A galvanic cell can form due to different temperature in the same metal
 - High temperature region more active → anodic
 - Low temperature region → cathodic

As a result of which you will find that more corrosion attack is there in the high temperature region. So, like that different examples are also shown here for example, different phases even of the same metal can form galvanic couple at the microstructure level like in steel cementite is noble as compared to ferrite. So, if you just take eutectoid steel of plain carbon steel of eutectoid composition. You will find that there will be due to the galvanic cell formation and also because of the galvanic corrosion, the ferrite part degrades or corroded to a large extent as compared to that of cementite part.

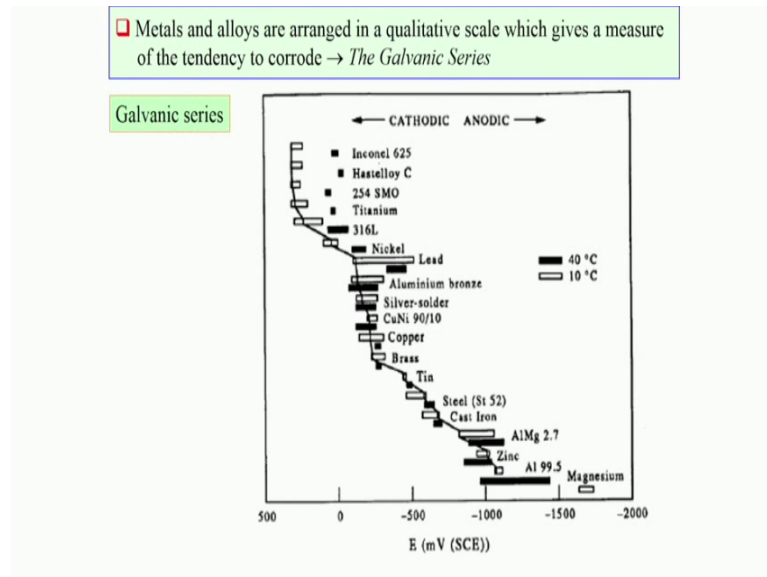
So, it may be formed by because of the concentration difference of metal ion in an electrolyte you call it concentration cell where metal ion deficit part act as anode and metal ion excess part act as cathode. Then you can also form that micro galvanic cell when there is a oxygen deficient region regime or oxygen enriched regime. For example, in case of previous corrosion you will find that the differential aeration cell formation is there.

Because of oxygen concentration difference which basically is nothing, but the kind of galvanic cathode. So, initiation starts because of the galvanic corrosion and then it proceeds thereafter to a large extent because of the auto catalytic reaction. Then galvanic cell wave form because of difference in residual stress as I mentioned you the stress region is more acts as anode as compared to that of stress free region. And galvanic cell may form due to difference in temperature in the same metal, like high temperature

region; high temperature region is more active usually acts as anode as compared to that of low temperature region.

So, if you take a component having different temperature in different region you will find that different temperature region basically corrodes to a different extent.

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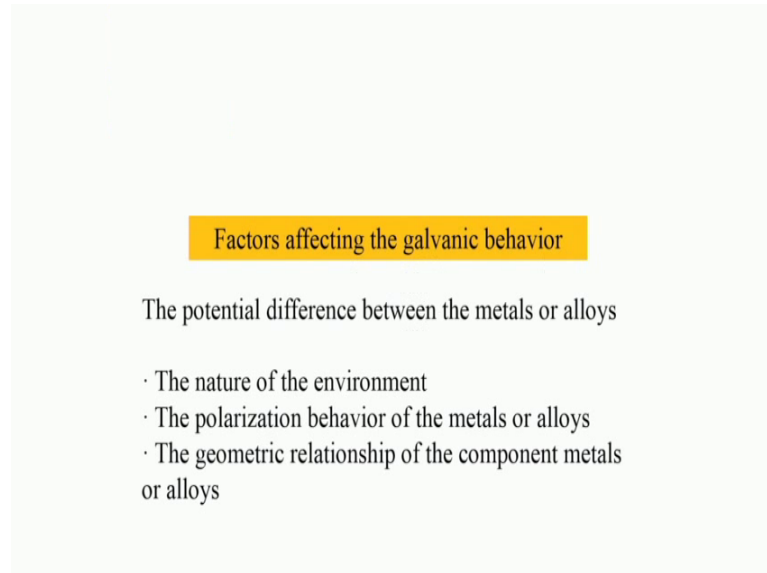
So, you have to be very much careful and in addition to that there is also the galvanic cells formation. So, as I mentioned you that galvanic series actually plays a very important role and also acts as a guideline for choice of material for galvanic coupling. So, whenever you have the necessity for application of two different metals or coupling of two different metals we just choose them which are more close in the galvanic series.

Like for example, the case for copper, nickel and silver solder if you are interested to just couple copper with copper nickel alloy that is very much acceptable. Copper can be coupled with brass as well, then tin can be coupled with brass there will be less a very less galvanic attack. But if you go on coupling steel with aluminium bronze or steel with nickel you will find that lot of galvanic attack will be there or a lot of corrosion will be there because of the galvanic corrosion.

Similarly, if you just choose zinc and if you just choose zinc and titanium or zinc and stainless steel you will find that there will be lot of galvanic attack. So, whenever you just go on choosing material combinations these galvanic series plays a very important

role to and acts as a guideline for the choice of the materials combination for a specific purpose.

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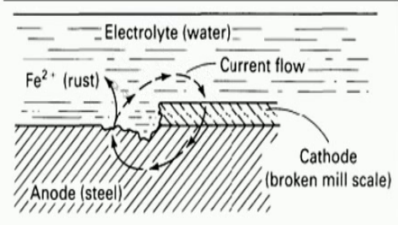


The slide features a light green background. At the top center, there is a yellow rectangular box containing the title "Factors affecting the galvanic behavior" in black text. Below the title, the text "The potential difference between the metals or alloys" is centered. Underneath this, there is a bulleted list of three items, each preceded by a small black dot. The list items are: "The nature of the environment", "The polarization behavior of the metals or alloys", and "The geometric relationship of the component metals or alloys".

Now, the factors which influence the galvanic behavior there ample for example, the potential difference between metals and alloys, so how they are basically placed in the galvanic series. Second part which is very important is that the kind of environment the component is exposed to because depending on the environment again, the position of different material or chemically reactive nation of different metal changes.

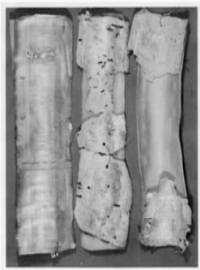
So, the environment which is actually the service environment of the component couple that also plays a very important role. Polarization behavior of the metals and alloys, geometrical relationship of the component metal or alloys and naturally temperature differences stress differences micro structures, these all factors play a very important role, play important roles actually to determine the galvanic corrosion behavior of the materials combinations.

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The schematic diagram shows a cross-section of steel with a layer of mill scale (Fe₂O₃) on top. A portion of the scale is broken, exposing the steel underneath. The exposed steel is labeled as the 'Anode (steel)' and the remaining scale is labeled as the 'Cathode (broken mill scale)'. The electrolyte is water. Arrows indicate 'Current flow' from the anode to the cathode. Fe²⁺ ions are shown moving from the anode into the electrolyte, where they form rust.

Schematic showing how breaks in mill scale (Fe₂O₃) can lead to galvanic corrosion of steel



The photograph shows three cylindrical metal samples. The leftmost sample is relatively smooth and shiny. The middle sample shows significant surface corrosion and pitting. The rightmost sample is heavily corroded, appearing dark and fragmented.

Galvanic Corrosion of Aluminium Shielding in Buried Telephone Cable Coupled to Buried Copper Plates

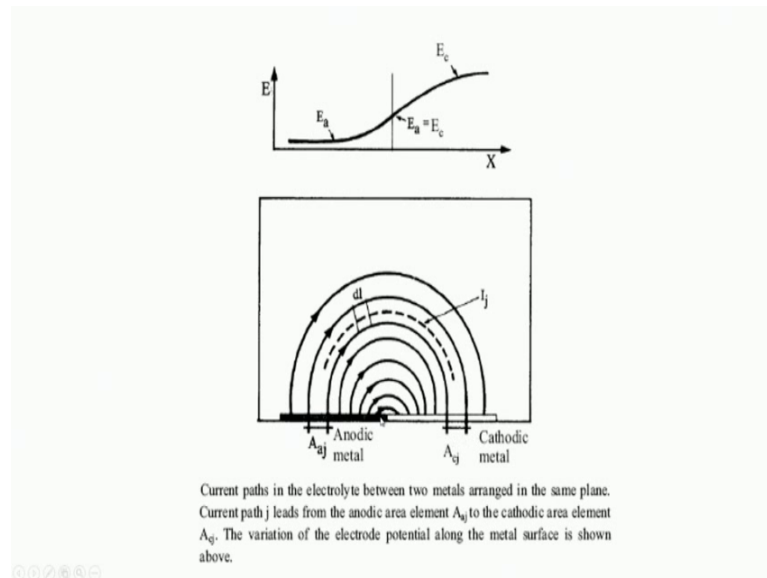


A small video frame in the bottom right corner shows a woman with glasses and a red top, speaking and gesturing with her hands.

So, this is see there are a few examples of the galvanic corrosion for example, this is the schematic showing break in the mill scale can actually there is a breakage of the mill scale and because of that naturally the fluid surface is exposed. And one surface is actually the it is steel there you will find the scale is still there, you will find that there is galvanic cell formation and as a result of which the in the broken surface or exposed surface the rate of attack is more than that of the unbroken part where scale is remaining.

Similarly, this is the case for galvanic corrosion of aluminium shielding in white telephone cable coupled to buried copper plates. So, we will find that at the particular that aluminium say copper is highly stable as compared to that aluminium, we will find that due to the galvanic attack the aluminium is basically destroyed to a large extent.

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So, current part in the electrolyte between two metals for example, if you have that anodic metal and then cathodic metal, so you will find that naturally the problem starts at the interface. So, the that anodic side basically corrodes to a large extent and by that process it protects the surface of the cathodic metals.

So, if you just go on measuring the like potential of the anode and cathode you will find that E anode is naturally quiet list this is active in nature any cathode is very high. So, you will find that from the interface the corrosion rate also changes.

So, near to the interface the corrosion rate actually is quite large and as you go on proceeding towards the anodic side naturally you will find that E corrosion is near to that of metal of with that E corrosion of the anode.

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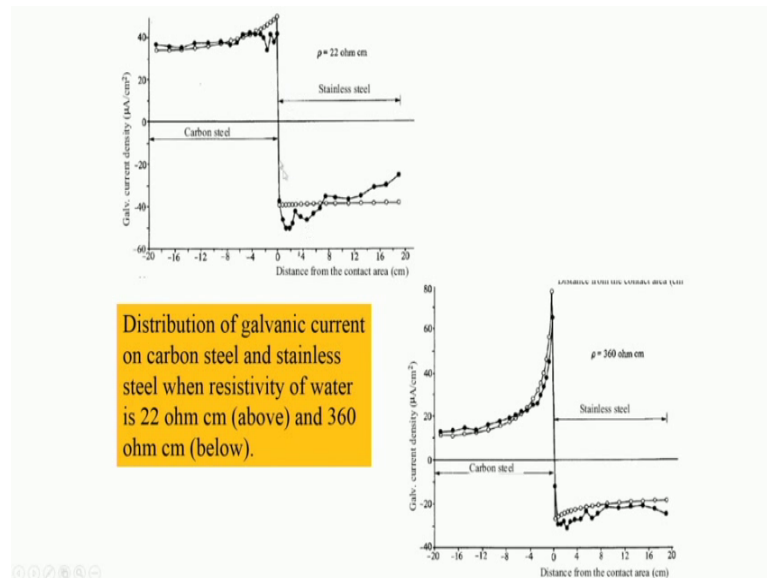


So, naturally you will see that usually that the interface plays is a very important role and everything, every problem starts from the interface. This is the galvanic corrosion of aluminium and copper coupling as I mentioned you, again galvanic corrosion of painted steel body steel auto body. So, you will find that there is by some way by erosion corrosion or by the typically the exposure of this particular painted surface to environment.

If there is a breakage of the or if there is damage of the paint layer you will find that there will be galvanic attack and this particular painting layer paint layer basically cannot safe the underlying metal because of the cathodic protection because paint is usually noble in nature. So, you will see that underlying metal actually corrodes to a large extent and rate of corrosion of the underlying metal is much higher than that of exposed part normally which is not painted.

Similarly, galvanic corrosion of steel pipe at brass fitting in humid marine environment you will find that where underneath that of kind of brass this thing there is a lot of corrosion in the steel and naturally you will find that this brass is noble are compared to that of steels. So, you will find that steel plate is or steel part is broken that damage to a large extent, as compared to that of the part where there is no connection actual rod there is no coupling.

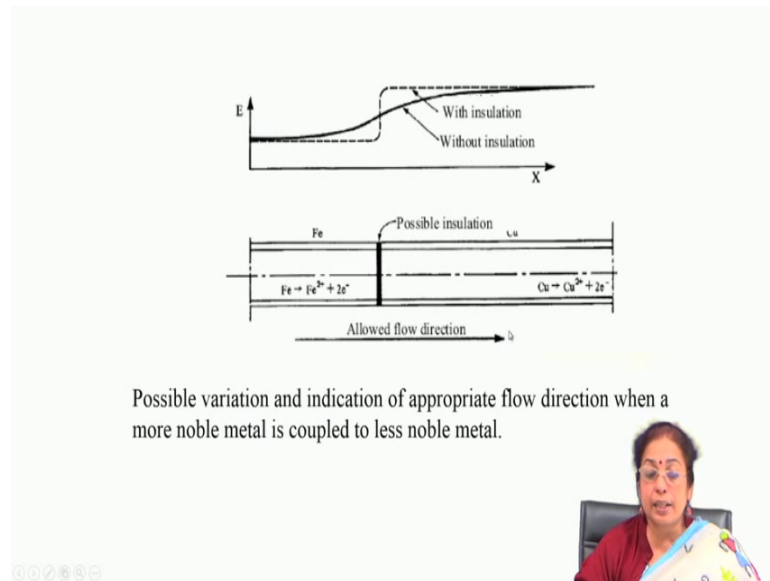
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This is the case for carbon steel stainless combinations, it also depends on you will find that carbon steel that this particular galvanic corrosion current density is much higher than that of stainless steel which is says basically non corroding in nature. And it also depends on the resistivity of the environment solution particularly.

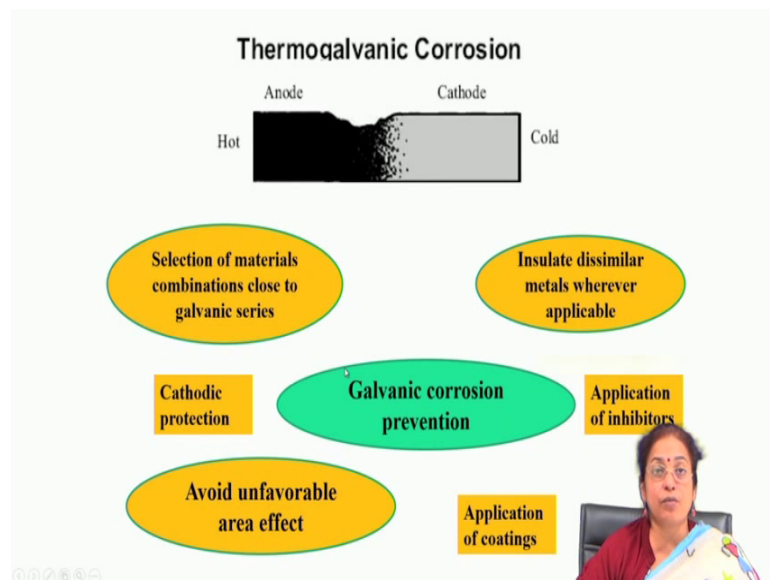
In water environment where resistivity is quite low here you will find that corrosion rate is much higher current density in terms of gravity current density as compared to that of the case where resistivity is very high. Resistivity of water naturally ionic conductivity plays a very important role and the conductivity of the electrolyte plays a very important role, higher is the ionic conductivity naturally higher will be the rate of corrosion atom.

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So, this is again flow (Refer Time: 14:05) again the combinations for iron and copper. So, you will find that if you go on insulating the part naturally you can minimize the tendency of the attack of the typical anodic part of the combinations of the couple.

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The this is the case for thermogalvanic corrosion where you find that hot part actually acts as anode as compared to that of cold part and problem starts at the interface. Now, if you quickly go through the way by which you can compare the galvanic corrosion.

So, usually the way or that techniques normally applied for prevention of general corrosion, some of the techniques are also applied or can be applied for the prevention of galvanic corrosion they are like cathodic protection, application of inhibitors, in the environment application of coatings. So, these are very standard way of protecting the surface for any kind of corrosion, but apart from that you can also choose the proper material combinations which are very close to the galvanic series, you can apply insulation in between the dissimilar materials.

And also another very important way of prevention of the galvanic corrosion is by avoiding the unfavorable area effect. So, usually corrosion whenever you talk about corrosion rate, current density is very important. So, if you have a very large area of contact of the anode as compared to that of cathode you will find that current density will be much lower. So, naturally as a result of which you find that degree of effectiveness or degree of corrosion will be reduced in the anode.

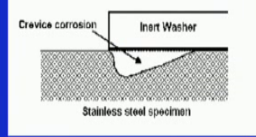
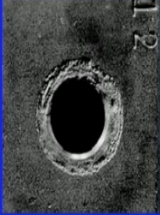
So, if you have a very large area can and cannot anode to cathode ratio you can reduce the probability or you can reduce the overall corrosion rate of the anode as compared to that of other way where you have very low anode to cathode ratio, very small area anode to cathode area ratio.

So, you have to avoid the unfavorable area effect actually. So, you have to whenever you have the possibility of galvanic coupling you choose the anode which is having much higher area then that of the cathode which is beneficial because it will reduce the current density and as a result of which corrosion rate of the anode.

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Crevice Corrosion

Crevice Corrosion occurs at shielded areas that contain a small volume of aqueous solution. Chlorides enhance crevice corrosion, but are not required.



Crevice corrosion of Type 316 stainless steel in acid condensate under a PTFE spacer. (Photograph by R. M. Kain, LaQue Center for Corrosion Technology.)

Typical schematic morphology with attack greatest at the mouth of the crevice. (From R. M. Kain, Metals Handbook, Corrosion, Vol. 13, 9th ed., ASM, Metals Park, OH, p. 109, 1987.)

D. A. Jones, Principles and Prevention of Corrosion, 2nd Ed., Simon & Schuster, Upper Saddle River, NJ (1996)

So, now III type of corrosion is the crevice corrosion. So, crevice corrosion is a kind of corrosion which occurs at the shielded areas that contain a small volume of the aqueous solution. So, usually when there is chloride in the environment it is basically aggravated, but it is not necessary to have the chloride in the environment. So, as I mentioned you that the galvanic corrosion, basically the crevice corrosion the process any processes or corrosion initiation mechanism is by galvanic attack.

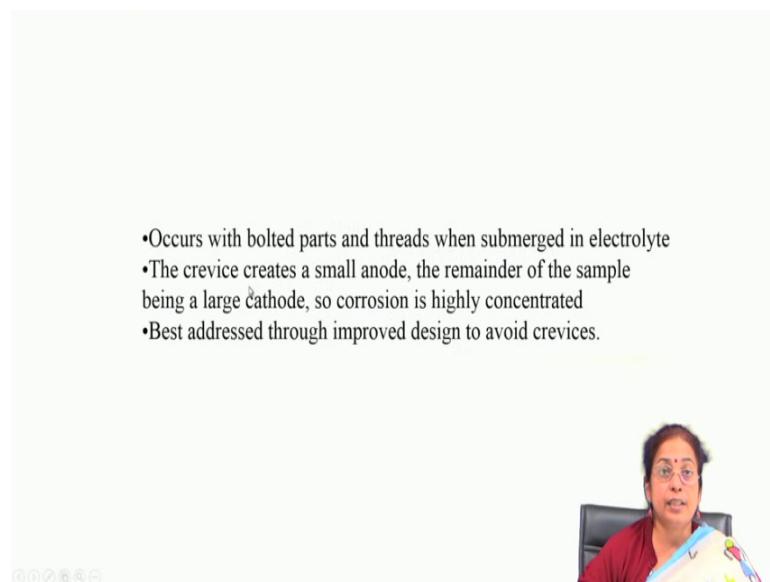
Because whenever there is a like shielded area you will find that in the inside the shielded area, the air concentration is much higher than that of outside shielded area. So, as a result of ways there is differential aeration cell formation and because of aeration different cell relation cell formation you will find that there will be galvanic attack at the interface between the higher region as well as lower concentration region.

So, because of that again galvanic cathode their (Refer Time: 17:35) corrosion starts and as soon as it starts you will find that in the crevice region where there is a electrolyte solution, but air concentration is not enough you find that there is no more the air the which is available is not adequate for the passive layer formation. And as a result of which you find that corrosion rate of the inner layer is much higher and it go on proceeding to a large extent as compared to that of outer layer, particularly because of the differential aeration cell formation.

And this particular case is by further aggravated if there is chloride in the environment because chloride they basically mitches the oxide film not only that chloride at chloride actually increases the corrosion rate to a large extent. So, presence of chloride is not really is dangerous where crevice attack is the main form of corrosion in engineering practice.

So, you will find that this crevice corrosion is observed in different not only in that shielded area, but also in any area where there is a for example, where you have washer and that is the loosely shielded actually, so they are also will find that typical crevice corrosion problem is existing.

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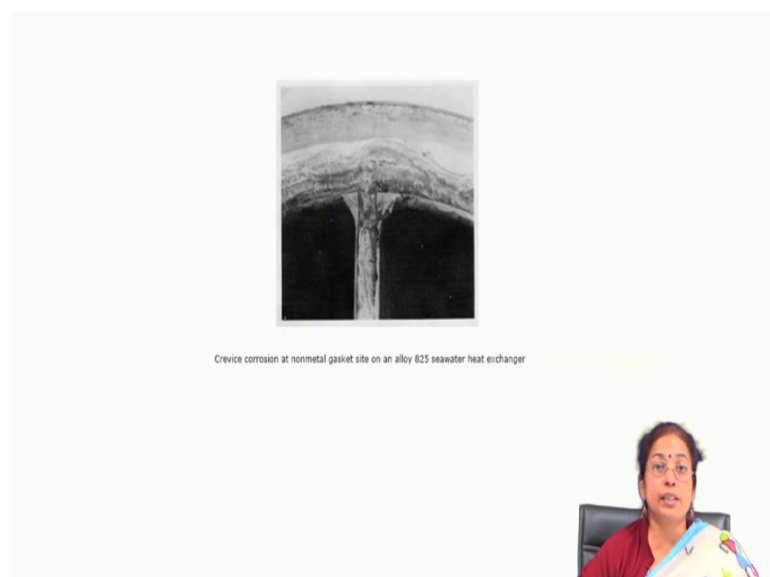
So, it occurs with bolted parts and threads when submerged electrolyte. The crevice creates a small anode and the remainder of the sample its being a large. So, here another problem is also there, not only the differential aeration formation, but also the unfavorable area ratio is also existing because if the crevice region the area is much lower than that of the outside region. So, because of the very low anode to cathode ratio you will find that or very small anode to cathode ratio the corrosion rate inside the crevice region is much higher than that of outer part.

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So, you have to be very much careful and design the component combinations properly, so that you can compare that possibility of the crevice attack. This is the example of crevice corrosion at a metal to metal crevice site formed between the components of type 304 stainless steel fastener in seawater. So, you find that lot of crevice corrosion is there at the in the fastener.

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Again crevice corrosion at nonmetal gasket site on an alloy 825 seawater heat exchanger. So, in the gasket you will find that because of the presence of gasket, usually that part

is actually they are crevice corrosion creates lot of trouble and it damages the surface to a large extend.

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Then crevice related corrosion for different alloys in natural sea water again you will find that lot of corrosion is there at the crevice site as compared to that of our surrounding region.

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Geometrical	Electrochemical reactions
Type of crevice: metal to metal nonmetal to metal Crevice gap (tightness) Crevice depth Exterior to interior surface area ratio	Metal dissolution O ₂ reduction H ₂ evolution
Environmental	Metallurgical
Bulk solution: O ₂ content pH chloride level temperature agitation Mass transport, migration Diffusion and convection Crevice solution: hydrolysis equilibria Biological influences	Alloy composition: major elements minor elements impurities Passive film characteristics

Factors influencing the crevice corrosion behavior of AISI 304 SS

So, if you just quickly go through their different factors or parameters which influence the crevice attack of a component, these are apples. For example, that type of crevice

whether it is metal to metal combinations or non metal to metal combinations. The gap and degree of tightness, the crevice depth, then exterior to interior surface area ratio.

Because as I mentioned you that these all factors play a very important role because if you see carefully the factors you will find that like type of crevice. So, there is metal to metal or nonmetal to metal. So, if it is metal to metal they are quite close to the this galvanic series, on the other hand if it is not metal to metal they are widely apart in the galvanic series.

So, you will find that probability of crevice attack will be more where when there is non metal to metal attack as compared to that of metal to metal attack. Again crevice gap is very important because the lower is the gap smaller will be the electrolyte and larger is the gap naturally higher visible with the electrolyte in the crevice side.

So, accordingly is fine that attack rate will also vary. Crevice depth is also very important, so where you are you find that as you go on increasing with depth or if you go on changing depth you will find that attack rate will be usually more actually because on the surface the attack rate is much lower because it is exposed to the environment. So, there is possibility of the layer oxide layer formation.

And as you go on decreasing, as you go on proceeding towards the depth you will find that there will be more less oxygen supply or less air supply as a result of which you will find that there will be the more tendency for the crevice corrosion. Then exterior to interior surface area ratio it basically controls the this is the basic principle of combating the galvanic corrosion, higher is the ratio of the anode to cathode naturally lower will be the crevice attack.

But lower is the anode to cathode ratio or smaller is the anode to cathode ratio, higher will be the crevice attack. Then if you talk about environment, then whether it is the how much is the oxygen content in the environment, how much is the pH in the environment, then chloride level, temperature, agitation these all play very important role. So, mass transport migration whether you there is any kind of stirring action in the environment, diffusion and convection whether any flow is there flow is whether laminar flow or convective dominated flow.

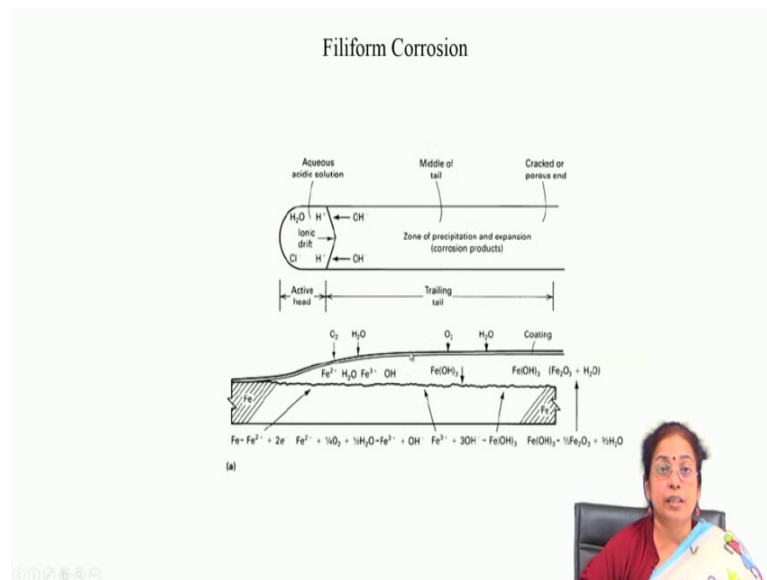
So, whether there is any biological influence sometimes we say the microbiological species if they are in the environment, they basically get accumulated on the surface and it acts as a site for the crevice corrosion initiation. So, as you if you do not clean it properly you will find that after a while there will be lot of crevice attack and you have to be very much careful to repair the part otherwise there will be severe damage of the component.

If you talk about electrochemical reactions there metal dissolution oxygen reduction and hydrogen evolution. So, these are very important and also metallurgical phenomena or metallurgical parameters which are important they are nothing, but the elements or maybe the components that ingredients in the alloy. Whether any impurities are there, whether there are different phases in the particular alloy, then what is the passive field characteristics, whether passive field it should be stable or not stable.

For example, if you take that case for 304 stainless steel you will find that it is more prone to crevice attack as compared to that of 316 cells stainless steel or 316 variety of stainless steel which contains a little bit of which contains little bit of molybdenum. So, when molybdenum is there in that particular alloy you find that film is highly stable as compared to that of chromium chromic oxide film which basically protects the surface.

So, when that molybdenum is there it forms a complex oxide which is stable in that particular crevice environment or chloride containing environment which is more stable and basically it reduces the probability of crevice corrosion.

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So, one of the important form of crevice corrosion is filiform corrosion which usually is observed in the painted surface. So, what happens is there in the painted surface? There is always very small small nano level perforations or porosity is micro to micro level porosity is to nano level porosities.

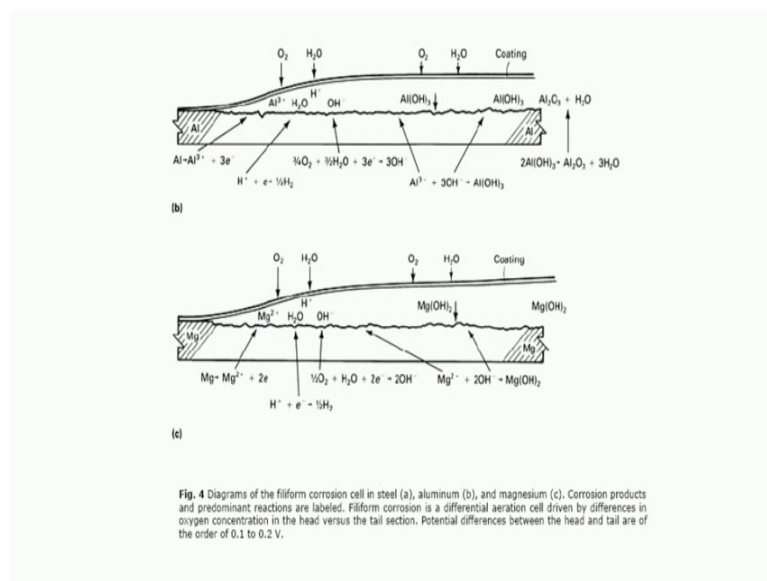
So, through the porosities there is always that water molecule absorption when the water molecule get absorbed on the surface, there is iron oxide formation ferric oxide and also ferric hydroxide formation and you will find that there is always concentration in the. Whenever if you talk if you see this particular formation probability or formation growth rate in different regions you will find that it is higher at some region some of the part of the region it is not uniform rather.

Because wherever there is perforation very small porosity is there through there only through that porous region only there is my iteration of the water molecule and then there is formation of iron and hydroxide. So, whenever there is hydroxide formation there actually there will be much more moisture absorption.

So, there is always a differential aeration cell formation and also the different phase formation like micro galvanic cell formation because hydrides are more stable as compared to that of ion which is there. So, as a result of which because of the galvanic cell formation and once that absorption these particular reaction proceeds from the from one side to other.

So, initially the attack starts at some region where there are small perforations or damage or porosities on the paint surface, but as soon as it forms the one end gets open and through that end there is water molecule migration. And then there is differential aeration cell formation and subsequently damage subsequently corrosion of the other part of the metal and this particular thing proceeds in a tubular fashion and you call it as filiform corrosion.

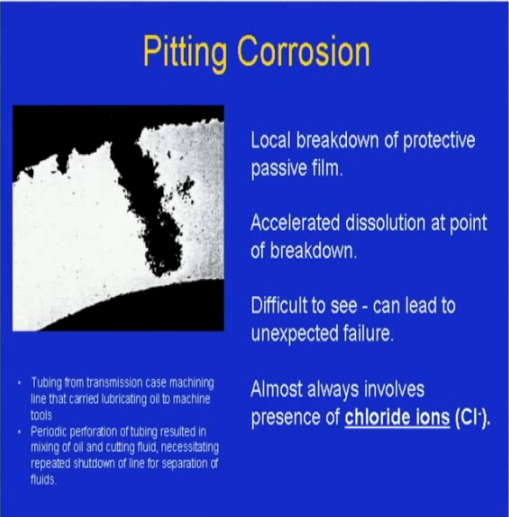
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So, when you look at the surface you will find that it basically the filiform for filiform corrosion basically, the appearance of the filiform formation is like in a tubular fashion zigzag zone on the surface.

This usually is observed in aluminium, magnesium, iron these all surfaces for whose hydroxides are very much prone to get hydrated or prone to absorb moisture and which is very much prone to form the which is very much prone which are very much prone to corrode in aqueous environment.

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Pitting Corrosion

Local breakdown of protective passive film.

Accelerated dissolution at point of breakdown.

Difficult to see - can lead to unexpected failure.

Almost always involves presence of chloride ions (Cl⁻).

- Tubing from transmission case machining line that carried lubricating oil to machine tools
- Periodic perforation of tubing resulted in mixing of oil and cutting fluid, necessitating repeated shutdown of line for separation of fluids.

So, another type of important corrosion is the pitting corrosion usually. So, that I will discuss in the next class, but before the beginning of the next talk I must say that crevice corrosion, galvanic corrosion these are very important kind of corrosion because they are basically localized in nature and whenever you talk about this kind of corrosion you have to be very much careful again to choose the proper material. If you talk about the prevention of the crevice attack, then you have to be careful in cleaning the surface at a regular interval you have to just avoid the conditions.

So, that there is no crevice gap, there is no crevice zone in the metal. So, you have to be very much careful to avoid shielding and also if you just flow the air properly or flow the water properly, so that region is properly protected then there is less probability of crevice attack. You can also get rid of the crevice corrosion by proper choice of material as I mentioned you the kind of film which forms on the surface it protects the surface to a large extent, then it can minimize the tendency of the crevice attack.

For example, the case of mild steel as well as stainless steel, 304 stainless steel and 316 stainless steel, if you just compare these three cases you find that the minimum crevice attack will be there in 316 stainless steel as compared to that of that mild steel or 304 stainless steel.

Because there is stable oxide formation which is highly stable even though there is a differential aeration cell formation, it basically does not get deteriorated even if there is

chloride in the environment it does not that chloride cannot bleach away the oxide layer which is forming on the surface.

You can reduce the possibility of crevice attack by reducing the temperature, by reducing the chloride level in the environment, by the application of inhibitors in the environment and also by cathodic protection. So, these are the different ways by which you can reduce the probability of the crevice corrosion.

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And finally, you have to choose the proper materials, so that you can get rid of this kind of corrosion to a large extend.

Thank you very much.