Corrosion Failures and Analysis
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Lecture - 06
Galvanic corrosion (Part 1)

Welcome back to the course. Today, we have 6 lecture for the course Corrosion Failures and Analysis. And today is 6th lecture, and topic we will start discussing on Galvanic corrosion.

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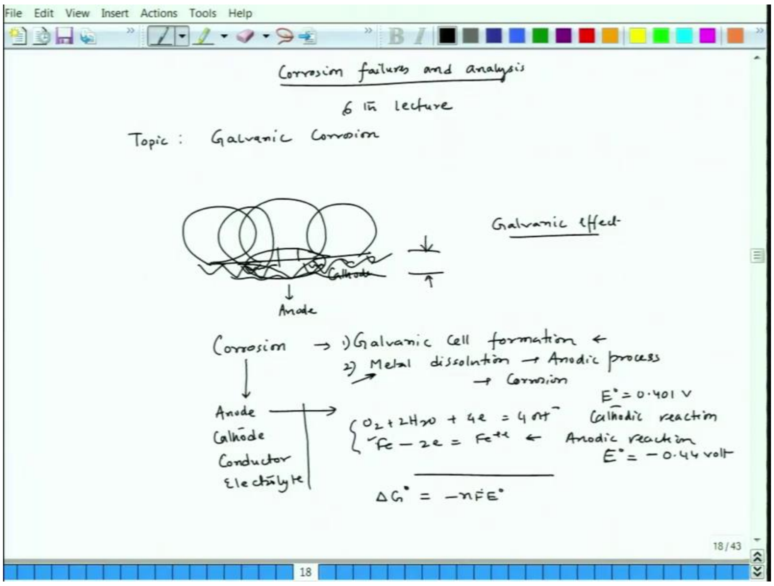

Corrosion failures and analysis

6 th lecture

Topic : Galvanic Corrosion

Galvanic effect

Corrosion → 1) Galvanic cell formation ←
2) Metal dissolution → Anodic process
→ Corrosion

Anode
Cathode
Conductor
Electrolyte

$E^\circ = 0.401$ V

$O_2 + 2H_2O + 4e = 4OH^-$ Cathodic reaction

$Fe - 2e = Fe^{++}$ ← Anodic reaction

$E^\circ = -0.44$ volt

$\Delta G^\circ = -nFE^\circ$

Now, if you see the uniform corrosion mode, and there you could find that cathodic and anodic reactions are taking place, and cathodic and anodic reactions are actually uniformly taking place over the entire metal surface. In fact, at the end of while we started looking at different aspects, different the mechanisms of uniform corrosions, we checked upped, we talked about rain droplet corrosion.

In fact, while talking about rain droplet corrosion, we mentioned that it is basically in a galvanic mode where cathodes and anodes are forming at specific locations, it is not happening at a over the entire surface covered by the droplet, ok. So, it is basically if you go back and see, this is the droplet, and we could see that the corrosion pattern is like this.

So, in the center part, we have the highest corrosion. And the center part is preferentially anode and the periphery region is preferentially cathode. And this happens because of the change in concentration of oxygen or the dissolve oxygen in the droplet around that periphery.

The around the periphery there is no change in the oxygen concentration, but in the center part of that particular droplet we have do experience oxygen depletion, and that for there is a change in concentration of oxygen and it leads to a concentration cell. And that concentration cell leads to this difference in corrosion behavior across this area, this area, across this area.

So, and we said that this is basically a corrosion cell, and that corrosion cell is leading to difference in corrosion; there are two segments and that cell actually leading to that particular typical formation of those cathodes and anodes, the center part is corroding more, and it is a localized effect is coming up. And we related this particular phenomena with the uniform corrosion saying that the droplet is also forming sometime here, sometime here, sometime here.

So, finally, those localized corrosions are actually connected together and then having a uniform mode, ok. So, this segment is basically uniformly corroding. But if you look at one particular droplet it is basically localized, the center part is having more corrosion rather than the periphery part. And this is a serious galvanic effect.

Now, question is whether uniform corrosion though as per the form we say that this is the uniform corrosion, but if you carefully look at the mechanism is nothing but the galvanic corrosion. Why? Why do you say that mechanism is galvanic corrosion? Because corrosion is nothing, but a galvanic cell formation, this is one. And the second part is metal dissolution is the anodic process.

And this is nothing but the corrosion, but as we know the corrosion has 4 parts, anodes or anode let us say anode, cathode, conductor and electrolyte, fine. So, these 4 parts out of that this talks about this particular phenomena, but otherwise all the parts are required otherwise corrosion may not take place, fine.

Now, coming to this galvanic cell formation let us see whether uniform corrosion is also a galvanic mode. Let us talk about iron corrosion what we have already explained. So, iron plate in air where moisture is present, so the cathodic reaction is nothing but H2O plus 4e; O2 plus 2H2O equal to 4 OH minus. This is the cathodic reaction. And then anodic reaction which is corrosion is plus 2.

$$O_2 + 2H_2O + 4e = 4OH^-$$

$$Fe - 2e = Fe^{++}$$

And these two reaction must happen together otherwise singularly this reaction cannot take place. And if we see that why this reaction continues, because if we consider their standard reduction potential for those two reactions, for the first reaction the standard reduction potential is volt and the second reaction E0 equal to minus 0.44 volt. So, these are with reference to hydrogen reference, the standard hydrogen electrode, ok.

Now, why do we have this reactions to continue? Because if we try to find out free energy change which is delta G0 is equal to minus n FE0, which is the E0 is the standard reduction potential for the cell.

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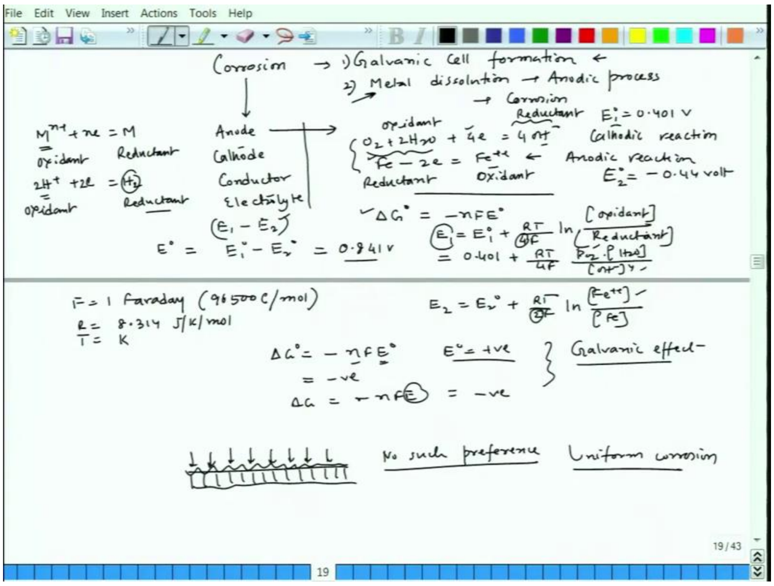

Corrosion → 1) Galvanic Cell formation ←
2) Metal dissolution → Anodic process
→ Corrosion

$M^{n+} + ne = M$
oxidant Reductant
$2H^+ + 2e = H_2$
oxidant Reductant

Anode
Cathode
Conductor
Electrolyte

oxidant Reductant $E_1^\circ = 0.401$ V
$O_2 + 2H_2O + 4e = 4OH^-$ Cathodic reaction
$Fe - 2e = Fe^{++}$ ← Anodic reaction
Reductant Oxidant $E_2^\circ = -0.44$ volt

$\Delta G^\circ = -nFE^\circ$

$(E_1 - E_2)$
$E^\circ = E_1^\circ - E_2^\circ = 0.841$ V

$E_1 = E_1^\circ + \frac{RT}{4F} \ln \frac{[\text{oxidant}]}{[\text{Reductant}]}$
$= 0.401 + \frac{RT}{4F} \frac{P_{O_2} \cdot [H_2O]}{[OH^-]^4}$

F = 1 Faraday (96500 C/mol)
R = 8.314 J/K/mol
T = K

$E_2 = E_2^\circ + \frac{RT}{2F} \ln \frac{[Fe^{++}]}{[Fe]}$

$\Delta G^\circ = -nFE^\circ$ $E^\circ = +ve$
$= -ve$ } Galvanic effect
$\Delta G = -nFE = -ve$

No such preference Uniform corrosion

And for this complete cell, the standard reduction potential E0 would be find out and let us see if it is E1, if it is E2, E10 minus E20 which becomes if they are in standard state, so which is impossible, but let us assume that this is the value what we have. In actual cases these values would be different. Remember because the iron and concentration may not be 1 and these concentration may not be also 1.

$$\Delta G^{O} = -nFE^{O}$$

$$E^{O} = E_1^{o} - E_2^{o}$$

$$E_1 = E^{O} + \frac{RT}{4F} ln \frac{[Oxidant]}{[Reductant]}$$

$$E_1 = 0.401 + \frac{RT}{4F} ln \frac{p_{O_2}.p[H_2O]}{[OH^-]^4}$$

$$E_2 = E_2^{O} + \frac{RT}{2F} ln \frac{[Fe^{++}]}{[Fe]}$$

So, that case the things will be these values would be different and that will be calculated on the basis of Nernst equation. And what is the what are the Nernst equation? For the reaction 1, Nernst equation would be E equal to E naught plus RT, and here the electron is 4, 4 F ln and we know that oxidant concentration divided by reductant concentration here, and oxidant part is in this case here this is oxidant, and this is a reductant. And here in this case, this is oxidant and this is reductant.

And how to recall? Whenever you have some difficulty in understanding which one is oxidant and which one is reductant write everything in reduction mode. For example, Mn plus plus ne equal to M, so that time this would be oxidant and this should be reductant. Or you just go to hydrogen reaction, and we know hydrogen is a very good reducing agent, hydrogen is a very good reducing agent, so this has to be reductant and this one has to be oxidant, fine.

So, now since we write this way. So, we can write this is 0.401 for the first reaction plus RT 4F, F is Faraday. Here what are the terms? F is one Faraday which is 96500 Coulomb per mol of electron, but this value is little different 96488 something like that, so we write it we round it off to and write it 49500.

And R you can take it as universal gas constant 8.314 Joule per Kelvin per mol, ok and temperature is in Kelvin, ok. So, now you can write partial pressure of oxygen because this is the oxidant into hydrogen water concentration and OH minus ion 4 to the power 4 and second case this is E1, this is E1, this is E2, E2 naught plus RT. Here the number of electrons involve is 2, ln, oxidant here it is iron iron and this is this is the equation Nernst equation.

So, now depending on the concentration here of that iron plus plus or depending on oxygen presence, partial pressure of oxygen and OH ion concentration in the solution or the electrolyte, we can have different E1 value. So, that time instead of E1, we have to write E1 minus E1 naught you have to write E1 minus E2, fine.

So, now, once you do that you will see so, that value would come 0.841 volt. And now if I apply this particular equation, we see that delta G naught is nothing but minus. So, now, in this case it will be this value, but if you take E1 and E2 this value then we have to take consideration of this particular number. So, that value would be different, ok.

Now, n FE naught, so n would be decided by equilibrated condition, ok. So, now, this E naught is positive, hence this would be negative, and we know if the free energy change is negative we do get the reaction to continue, ok. That means, the free energy change and if you take non-standard condition that time it this would be delta G would be minus n FE.

So, that time no standard values are to be taken. We have to calculate the actual value fine. So, if this time also this will become positive negative. So, that is what this both this reaction will continue if we have supply of oxygen as well as there is a huge source of iron because the iron plate is corroding.

So, now this particular effect is nothing, but the galvanic effect. So, this is coming from galvanic effect and this is a typical electrochemical galvanic effect. So, that means, here the iron corrosion is actually a galvanic corrosion. But interestingly the form is uniform because this galvanic corrosion is taking place over the entire iron surface, so that means, this is the iron surface.

So, everywhere we are getting this both these reactions and there is no specific localized cathodic or anodic reactions. So, it is a basically, just like for example, in this case droplet case we see that the peripheral part is preferentially cathode, the center part is preferentially anode, but there is no such preference. Hence, the corrosion is taking place uniformly over the entire cross section. So, that is what we call it uniform corrosion.

So, galvanic uniform corrosion from the fundamental mechanism point of view is actually galvanic corrosion if you consider the electrochemical reaction part. But since it is happening over the entire surface without having any localized positioning of cathodes or anodes that is what we call it uniform corrosion. But theoretically, if we consider reaction wise its galvanic effect.

But if we come to galvanic corrosion part only, we would see that the galvanic effect comes specifically what we call it as a galvanic effect that when we have preferential locations of cathodes and anodes preferential locations of cathodes and anodes, ok. So, this is extremely important aspects.

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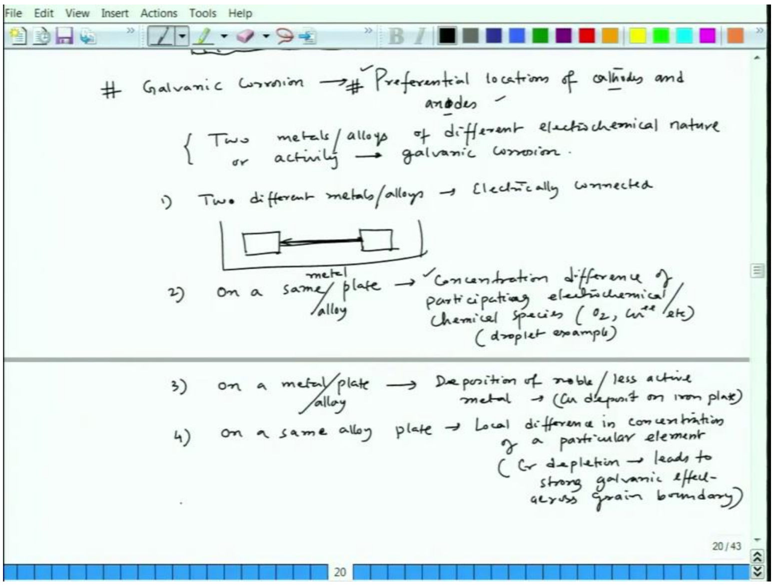

Galvanic Corrosion → # ✓Preferential locations of cathodes and anodes ✓

{ Two metals/alloys of different electrochemical nature or activity → galvanic corrosion.

1) Two different metals/alloys → Electrically connected

2) On a same metal/alloy plate → ✓Concentration difference of participating electrochemical/chemical species (O_2, Cu^{++}/etc) (droplet example)

3) on a metal/alloy plate → Deposition of noble/less active metal → (Cu deposit on iron plate)

4) on a same alloy plate → Local difference in concentration of a particular element (Cr depletion → leads to strong galvanic effect across grain boundary)

Now, whenever we talk about preferential locations of cathodes and anodes it can happen on the same plate due to concentration effect that is what we have in the understood in the rain droplet example or it could happen some metal deposition. And that metal deposition can happen because for example, if we talk about one example I have cited that is the copper deposit on the steel plate and that copper deposit can lead to a galvanic effect, ok. So, that is also there.

So, those part we will talk about later that how come this preferential location effect would come, and preferential locations of cathodes and anodes. But let us understand from the definition point of usual textbook what is written, they say that galvanic effect comes when two metals or alloys of different electrochemical nature or activity leads to galvanic corrosion.

Here they only talk about metals and alloys, fine. But we will see that it is not only specific to metals and alloys there are effect due to concentration also, fine. So, there the same galvanic effect can appear on a same plate without having different metals. Now, but this is a very very common definition you will find in many books, I mean almost all the books on corrosion fine.

Now, first understand this and then we will get to this part, ok, preferential locations of cathodes and anodes. And in fact, this preferential locations can come, ok if we since we have talked let us understand that what are the situations preferential locations comes if we take note of that.

One is, of course, usual definition, two different metals alloys there, and interestingly one part I missed is electrically contact connected. For example, if one metal is here another metal is here and they are in electrolyte, until unless they are in electrical electrically connected you hardly you do not experience galvanic effect, ok which actually relates to preferential locations of cathodes and anodes, ok. This galvanic effect would come when they are electrically connected, fine. So, this is one.

Second part is what we have understood if we see droplet is basically coming on a same plate concentration difference of participating electrochemical species, electrochemical or chemical species, it can be either let us say oxygen, copper ion, etcetera they can lead to galvanic effect. So, that would lead to preferential location of cathodes and anodes, ok. So, this is extremely important, fine.

Now, there could be possibility of on a plate, same plate, and whenever I am talking about my same plate the metal plate, there could be possibility of deposition noble or less active metal.

There could be possibility of, on a same plate there could be or in this case metal rather instead of metal I would say alloy plate and here all the cases you can put alloy and here also alloy, but here I am putting only alloy, ok. So, there could be local difference in concentration of a particular element, fine.

For example, this one, we have already seen the droplet experiment, droplet example. This one, we have we will explain again that is copper deposit on iron plate and this one we have touched it upon, but we will discuss more when we talk about inter granular corrosion, we will see that the chromium depletion leads to strong galvanic effect across grain boundary.

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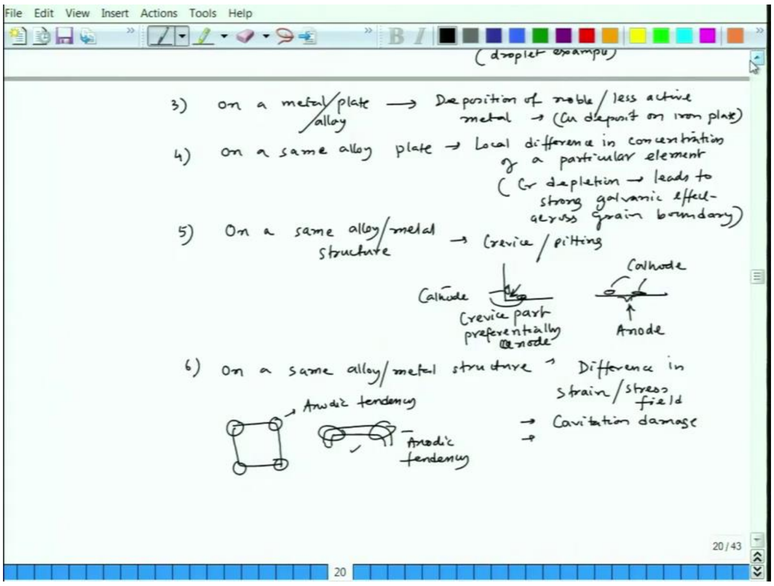

(droplet example)

3) on a metal/plate/alloy → Deposition of noble/less active metal → (Cu deposit on iron plate)

4) on a same alloy plate → Local difference in concentration of a particular element (Cr depletion → leads to strong galvanic effect across grain boundary)

5) On a same alloy/metal structure → Crevice/pitting

Cathode
Crevice part preferentially anode
Cathode
Anode

6) On a same alloy/metal structure → Difference in strain/stress field
→ Cavitation damage
→

Anodic tendency
Anodic tendency

There could be effect due to crevice rather on a same alloy or metal structure. You can have crevice or pitting that could also lead to a strong galvanic effect. We will see later. For example, if this is the crevice you will see that this crevice part or if it is a pitting, let us say this small pit has formed, the pit part this will be preferentially anode, and this, and here also this crevice part would be preferentially anode and around that section will be preferentially cathode.

And here also, around this crevice part you will see these are cathode. So, again there is a situation of preferential anodes and cathodes. So, again coming back to this particular statement this is extremely important while understanding galvanic corrosion, fine.

So, that means, these are the normally observed practice, observed situation, we could get preferential anode. And for example, one such example let me just show you. For example, on a same alloy or metal plate structure there could be difference in strain or stress of stress field and that could also lead to preferential positioning of anodes and cathodes.

And this, one such example will talk is about cavitation damage. Or in case of stainless steel, we will also see that if the strain relief operation is not done, so that is not particular related to this. But at least on a same structure sometimes at one location you could find that is strained heavily and another location it could you could find that is not strained heavily. I will also show one such example. I have that particular rod; if you and also you can also go back and check on the roads.

On the roads, you will find that reinforced bars, reinforced bars are actually made into a kind of this kind of shape, ok a square shape. Or sometimes you would find in the household application some object is bent. And whenever there is a bend, this bent location these are extremely strained. So, that location has the preferential anodic tendency. So, this is preferential anodic tendency, fine.

So, then also you can get galvanic effect on those corners part. So, this particular one thing I will show it in the next lecture, next class, ok. You will see that there I have a rod, I have collected from the road side, and you will see that on the bent portion the corrosion is concentrated and that actually happens because of that strain effect, ok.

So, these are a common problem, we will discuss more on this as we go ahead. But at least you should appreciate that whenever we talk about galvanic corrosion from the definition wise it is not only two metal or two different metals or alloys which are electrically connected exposed to an electrolyte, but at the same time you can have that galvanic effect because of other reasons without having two metal contacts, ok, two different metal contacts.

So, let me conclude here that galvanic effect is actually due to preferential location of cathodes and anodes, not only two metal contacts. So, that is what I would like to stress upon here. So, we will continue our discussion in our next lecture.

Thank you.