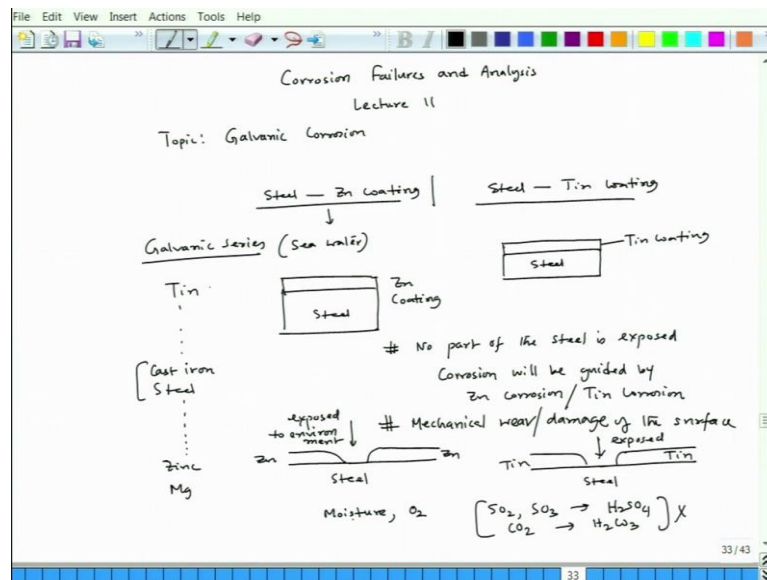


Corrosion Failures and Analysis
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 11
Factors associated with galvanic corrosion: Case study 1

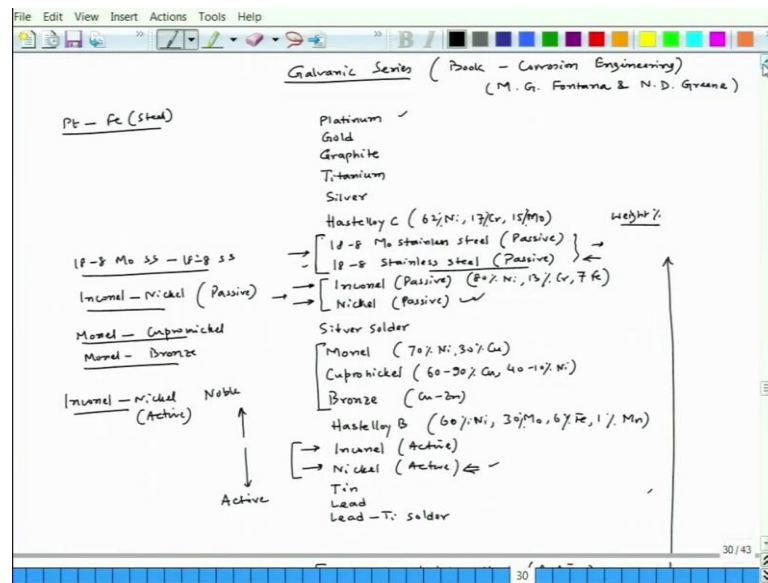
Welcome back to the course Corrosion Failures and Analysis, and we have lecture 11 now, and the topic covered will be galvanic corrosion. We have talked about galvanic series as well as mechanism of galvanic corrosion. Now gradually we will get into different Factors associated with the galvanic corrosion.

(Refer Slide Time: 00:43)



So, the course is corrosion failures and analysis and lecture 11 and the topic Galvanic Corrosion. Now, we talked about galvanic series. And if I go back to that galvanic series, again.

(Refer Slide Time: 01:23)



If you see this, this galvanic series is basically, it is a mention of all the metals and alloys and the metals which is sitting above will act as anode cathode and metal which is sitting below which will act as anode. And interestingly, this galvanic series what is mentioned in that book, it is basically in sea water; it is in sea water, ok. So, now if you change that electrolyte, it might change again.

So now, in that galvanic series, we talked about cathodic protection; in that cathodic protection, one is sacrificial, one is the cathode which is being protected, for example, we talk about steel and zinc coating. Now, if we have zinc coating, now steel; another situation tin coating let say, tin coating fine. So, these are the 2 situations let us consider.

And let us look at their positions. And if I see the positions, you just go back in the previous lecture you can see that in the galvanic series what has been taken from the book by written by Fontana and Greene.

So, there it is in the sea water, tin is on top of steel and in between there are quite where a good number of metals and alloys. For example, we have lead, lead tin solder in between tin and steel; then active 18-8 stainless steel, then we have cast iron. In fact cast iron is basically in the bracketed form, so that means cast iron steel can be considered as a grouped one. So, where if you have a cast iron and steel combination so galvanic effect will be minimized.

Now, again if we see zinc presence in between we have good number of aluminium, cadmium, commercial pure aluminium and then we are having zinc. And in fact below that zinc, we have put magnesium, ok. So now, here the combination is, we have a steel plate and then we are putting a tin coating. So, this is the tin coating let say. In another case, in this case this is steel; in this case steel and on top of that we have zinc coating, ok.

Now, when they are intact, so that means no steel is exposed; no part of the steel is exposed. So, the condition one is no part of the steel is exposed, ok. Now if no part of steel is exposed, then zinc will corrode on its own nature in sea water and tin will corrode on its own as it is its own electrochemical character in sea water.

In fact in normal atmosphere also tin stays on top of steel and zinc stays below tin steel. You know that time the corrosion will be guided by zinc corrosion or tin corrosion, ok. So, that is the situation.

But now question is, if zinc corrosion and tin corrosion is taking place until unless the steel is exposed, how come the effect of galvanic corrosion comes in? Now, question is whenever it is coated and it is transported or when it is loaded and unloaded; loaded at factory end and the unloaded at the customer end, there will be always some mechanical erosion or mechanical wear.

And that mechanical wear or damage of the surface; even let say there is no damage, but still when you fix that steel sheet coated with zinc. When you fix it on the roof, we have to also puncture it and then fix nuts and bolts to fascinate with the structure we are making beneath the roof. So, that time we are actually making perforation. And what happens because of that; some part of it, some part of this is steel and this is zinc, this is zinc; some part of a steel is exposed to environment.

Similar thing can happen here, steel is exposed, ok. Now, because of this exposure to the electrolyte, there could be moisture; let say there is some moisture present, because it is environment, lot of moistures are present. So, we have moisture and of course in the environment, we have oxygen. Let us not take other substance acid forming substance like SO_2 or SO_3 which will lead to H_2SO_4 or let say carbon dioxide which can form carbonic acid, ok.

(Refer Slide Time: 08:55)

The whiteboard contains the following content:

- Top Left:** A diagram showing a cross-section of a steel plate with a zinc coating. Labels include "Tin", "Zinc", "Mg", and "Cast iron Steel".
- Top Right:** A diagram showing a cross-section of a steel plate with a tin coating. Labels include "Steel", "Zn Coating", and "Tin".
- Chemical Equations:**
 - (c) $O_2 + 2H_2O + 4e^- = 4OH^-$
 - (a) $Zn - 2e^- = Zn^{2+}$
 - (c) $O_2 + 2H_2O + 4e^- = 4OH^-$
 - (a) $Sn - 2e^- = Sn^{2+}$
- Text:** "No part of the steel is exposed", "Corrosion will be guided by Zn corrosion / Tin corrosion", "Mechanical wear/damage of the surface exposed".
- Diagram:** A cross-section showing "Steel protected (Cathodic)" and "Tin exposed".
- Chemical Equations:**
 - $[SO_2, SO_3 \rightarrow H_2SO_4]$
 - $[CO_2 \rightarrow H_2CO_3]$
- Bottom Section:**
 - (Zn - Steel) Cathodic reaction $\Rightarrow O_2 + 2H_2O + 4e^- = 4OH^-$ (Steel surface)
 - Steel - Cathode
 - Zn - Anode
 - $Zn - 2e^- = Zn^{2+}$ (Zn surface) \downarrow Protected dissolve (Anode)
- Diagram:** A cross-section showing "steel" and "protected steel".
- Page Number:** 33/43

So, let us not take those cases. Let say those are not there, only moisture and oxygen. And if the environment is neutral, then the cathodic reaction that would happen is; this cathodic reaction would happen. Similarly, now this cathodic reaction would happen, where it would happen now we have to judge. Now, as per galvanic series, I could see that the steel is staying on top of zinc. So here the cathodic reaction happen on iron or steel surface, ok.

Now, before this section was exposed, when no part was exposed the cathodic reaction was the same cathodic reaction was there; same cathodic reaction was there. An anodic reaction was zinc minus 2 equal to zinc plus plus, but those were happening over the entire segment and zinc was having uniform corrosion.

Similarly here, on top of tin, this cathodic reaction is, this is cathodic, this is anodic and here also cathodic reaction would be $O_2 + 2H_2O + 4e^- = 4OH^-$. An anodic reaction would be $Sn - 2e^- = Sn^{2+}$. So, dissolution of tin and dissolution of zincs are taking place over the entire surface uniform corrosion.

But once this steel part is exposed, this reaction would happen on steel surface in case of zinc steel situation. So that means in this case, not in this case; in this case this would be the situation, because as for the galvanic series, steel is cathode and zinc is anode, ok. So and cathodic reaction happens on cathode and cathode will be protected; though corrosion will be there, but that corrosion of steel will be very very small.

So, there will be little corrosion of course. So, you can have little bit of corrosion ok, iron corrosion. But this segments, these segments, so zinc section they will supply electron, this electron by this reaction, ok. So, this would happen on zinc surface, fine. And that way we will have electron supply and zinc is dissolving; dissolve or corrode and steel sections will be protected. So, the corrosion would be around that zinc part and but this one would be this segment will be protected.

An interesting part is, if this opening is quite large; let say the opening is quite large; instead of this, the opening is this. A quite a large segment of that steel surface is actually exposed to the environment. And that case you might experience that the corrosion in this particular steel segment will be more around centre part away from this joining part.

So, this segment will have more corrosion and this segment will be protected, but this segment will be less protected; less protected. Now, at least let us understand first this part; this part is understood that, because it is acting as cathode. So, that is what it is having less corrosion and zinc is sacrificing it itself. This particular example I will talk about in little while, first let us see the second part.

(Refer Slide Time: 13:51)

$(Zn-Steel)$ * Cathodic reaction $\Rightarrow O_2 + 2H_2O + 4e^- = 4OH^-$ (Steel surface)
 Steel - Cathode
 $Zn - 2e^- = Zn^{2+}$ (Zn surface) Protected
 $Zn - 2e^- = Zn^{2+}$ - dissolve (Anode)

$(Ti-Steel)$ * Cathode - Ti
 * Steel - Anode
 $O_2 + 2H_2O + 4e^- = 4OH^-$ (Ti surface)
 $Fe - 2e^- = Fe^{2+}$ (Steel surface)
 Fe - Sacrificial anode (Corrosion)

Diagram: A cross-section of a joint between Zn and Steel. The Zn part is labeled 'Zn' and the Steel part is labeled 'Steel'. The Zn part is shown as the 'Anode' and the Steel part as the 'Cathode'. Arrows indicate the flow of electrons from Zn to Steel. The Zn surface is labeled 'Zn - 2e^- = Zn^{2+}' and the Steel surface is labeled 'O_2 + 2H_2O + 4e^- = 4OH^-'. The Zn surface is also labeled 'dissolve (Anode)' and the Steel surface is labeled 'Protected'.

Extremely high Corrosion of steel \Rightarrow Large area of Cathode
 Small area of anode

Requirement of electrons for the cathodic reaction on large area cathode will be met by large amount of ion formation from small area anode \rightarrow High corrosion rate of anode

Thumb rule : 1) Choice of metals/Alloys \rightarrow They should stay close in galvanic series
 2) Area of Cathode $<$ Area of anode

34

The second part which talks about tin steel situation, ok. So, that time if you see this galvanic series; in case of tin and steel, tin will act as cathode now and this is tin and steel will act as anode, ok. So, cathodic reaction, here the cathodic reaction would be

this; this should happen on tin surface and that time that electron would be supplied by this one, which is steel surface steel surface.

So, in the second situation in fact steel is corroding, this is the steel corrosion part and the tin is protected. Though there will be little corrosion of tin, because we cannot stop corrosion for the tin the way we have explained our mixed potential theory in case of zinc and iron; you just go back and just have a look at it. Tin will corrode, but it will be less. But that corrosion also will be very small ok for the case of tin, but steel would corrode.

Now, interesting part is, in this case another effect would coming. It is very clear that now iron is acting as a sacrificial. This is acting as a sacrificial anode and this is nothing but same as zinc in case of zinc iron, ok. So, this is corrosion. But interesting part is, in this second case in this case iron corrosion would be extremely large, very large corrosion would happen. Why? Now, question is why; the very very extremely corrosion of steel. The reason lies on another factor.

Now, these cathodic reaction, this cathodic reaction happens on the entire surface. And in this case, the cathodic reaction happens on the small segment, fine. Now, since for example in this case if it hundred numbers of this reactions happens. In this case since the area of the cathode is very large, so this number could be thousand. So now, if it is thousand number, then where from that electron; even if it is hundred, where from that electrons will come? Electrons will be provided by the cathode anode section.

In this case, in case of steel zinc; zinc area is so large, so that much of electron will be supplied uniformly, let say it is happening uniformly, very little zinc will dissolve in order to protect steel. But since here we have a huge amount of cathodic reactions that are taking place on the tin surface. So that much of electron will be supplied with this narrow area, this narrow area will supply that electron.

And you know whenever it supplies that electron, large number of iron ions must form in order to supply this electron to this cathodic reactions. So, that requirement leads to a extremely high corrosion in this situation, in this situation ok; very very high corrosion; high rate of corrosion.

We will analyse it on the basis of mixed potential theory, but that I will do in the next lecture because we do not have much time left for this particular segment. But, at least let us analyse this part that, just by changing the galvanic series metals, the choice of metals we could see in one case it is actually sacrificially protected and in another case this another the same metal, same steel is actually behaving like a sacrificial anode.

So, in case of tin steel couple, steel is sacrificial anode; in case of zinc steel couple, zinc is sacrificial anode. And there steel is protected, but in this case steel is corroding very high. At the same time this extreme large corrosion of iron exposed steel part is coming due to large area of cathode, ok.

So, this large area of cathode and if we compare the area ratio; large area of cathode and small anode and the requirement of electrons for the cathodic reaction on large area cathode will be met by large amount of ion formation from small area anode. And that leads to high corrosion rate of anode.

Now, it is not only galvanic couple, the wrong galvanic couple. So, this is a wrong galvanic couple; the steel what is the actual structural material. We should not use some coating which is cathodic to that particular steel. But it also associated with the large area and small area; large area cathode and small area anode.

In the first case since; see, whenever we are using zinc coating we should not have such situation that the coating dissolves so quickly that we have to; the protection provided by that zinc coating is there only for few years. We want this particular steel to be protected for at least 10 years, ok.

So, that time that self-corrosion of zinc should also be minimized and that minimization is not coming just due to zinc corrosion; it is also coming because the anode area is very large and to protect that small cathode area, little electrons are required.

And that little electrons can be supplied by that zinc area and that little electron with zinc corrosion will be distributed over the surface. So, the net corrosion or of zinc would be less, just to give the same degree of protection and that is what the zinc coating will stay for longer duration.

But, if we see this particular situation, it is reverse happening; first of all, because the polarity is different, tin is cathode and small area steel is anode. But that area factor is also leading to extreme high corrosion of that particular small area anode. Now, the thumb rule is while ever whatever design you have the thumb rule is.

First thumb rule is; we should choose choice of metals or alloys, from they should stay close in galvanic series and the second thumb rule is area of cathode should be less than area of anode. So, then only we have good protection, otherwise it will just damage that.

Now, just let us explain this part. Now, whenever we have the; if we have for example, in this case it is zinc and this is steel section. Instead of a small area opening, this is steel and this is zinc and this is zinc.

Instead of small area opening, if it is the opening area is very large, then here also the steel will act cathode, act as cathode and zinc you will act as anode. But that electron flow, if we see the electron flow; so here we have this reaction, this reaction and that electron, this 4 electron will come from here to there ok; and by this reaction, ok.

Similarly, here of the same situation would happen. This reaction is happening here and this reaction would happen here. Now, electron or the current; so this electron flow, the rate of electron flow we convert into current. And here the current is actually flowing through that conductor and here the conductor is nothing but the metal conductor which is zinc and iron. And this current value, the current always chooses path of less resistance.

Now, if this the here also we are having this reaction. This reaction here also the centre part is also taking place, but for this, electron has to move from this to this, so quite a large part. Now, that electron would face resistance even if it is highly conducting, still it will face resistance by the conductor. So, the electron flow would be easier if it is close by this reactions are happening close by, rather than they are happening at a wide apart positions.

So, zinc corrosion, a zinc dissolution in the form of ions, the electrons that is generated may not go there. But still this reaction is happening, because it is exposed to the environment. Now, who would supply that electron? In fact, around that zone, the reaction that would happen is; so this reaction would happen. And this reaction would

happen around this zone, around this section and then this electron would be supplied there.

So, if we have written, if we write this plus 2; this electron would go there and it will meet the requirement of electrons for that cathodic reaction. So, in that case what situation we are coming up that, electrons would like to flow to a section, where the resistance is less.

Similarly, if we consider resistance is less. So that means if that galvanic couple is close by; that close by portion electron supply would be very easy, but wide apart the electron supply would be minimized.

And then corrosion protection, because of the sacrificial effect will be felt more around this part, around this segment, around this segment. Here also it will be felt, around this segment, but in this segment it will be it is iron it is own corrosion, which is meeting the requirement of electron for the oxygen reduction, ok.

So, that means if it is the good amount of area of steel is exposed because of the mechanical damage; then the galvanic effect would be felt minimum ok. Galvanic corrosion protection effect will be minimized and then centre part will be highly corroded.

But what one important thing we are getting that, if the galvanic couple is formed, around that couple we have the galvanic effect. The feeling of the galvanic effect will be felt more in that particular region, where the couple is joined together; away from that join the galvanic effect will be minimized, will be less; as you go away from that.

(Refer Slide Time: 28:00)

$Fe - 2e = Fe^{2+}$
 $Zn - 2e = Zn^{2+}$
 $O_2 + 2H_2O + 4e = 4OH^-$ (Tin surface)
 $Fe - 2e = Fe^{2+}$ (Steel surface)
 Fe - Sacrificial anode (Corrosion)

* Cathode - Tin
 * Steel - Anode

(Ti-Steel)

Extremely high corrosion of steel \Rightarrow Large area of Cathode
 Small area of anode

Requirement of electron for the cathodic reaction on large area cathode will be met by large amount of iron formation from small area anode \rightarrow High corrosion rate of anode

Thumb rule : 1) Choice of metals/Alloys \rightarrow They should stay close in galvanic series
 2) Area of Cathode $<$ Area of anode

Galvanic effect will be felt where joining of two metals/alloys is done

So, this is another important aspects we are learning from this example that; galvanic effect will be felt where joining of 2 metals or alloys is done, fine. Away from that joining, galvanic effect will gradually it will reduce, the way we have given this example, ok.

So, we will see that 2 effects; one is of course area factor, we have to see that area of cathode should be minimum less than the area of anode, so then corrosion effect of that anode would be less. And second part is, we have to also see that close to that galvanic point galvanic joining point, we feel the corrosion effect more and that basic effect.

Now, you can understand, why all the time whenever I have I show that corrosion effect in the galvanic mode, I have shown that the corrosion gradually reduces as you go away from the galvanic couple. That is the reason that the corrosion will be felt more in that galvanic joint portion, because this is the joining, this is the joining, around that joining portion galvanic effect will be felt, but away from that it will be minimized.

So, let us stop here. We will continue our discussion in our subsequent lectures.

Thank you.