Corrosion Failures and Analysis

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Lecture - 29

Various conditions favouring pitting corrosion (Part 1)

So, let us start lecture 29. The course is Corrosion Failures and Analysis, and we will discuss Pitting Corrosion. If you recall our last lecture, we started discussing about pitting corrosion. And we saw that if it is a passivating metal, pitting corrosion tendency becomes very prominent or becomes very obvious sometimes, not all the time remember. But passivating metal has that pitting tendency.

Stagnant solution is a problem, because that leads to pitting. And also, we have seen that the pitting happens on a flat surface. We do not need any crevice. In case of crevice, corrosion we need to have a crevice to have crevice corrosion, but pitting it can also happen on a flat surface. And many a times, before it is realized that the pitting has happened, the pit might have grown a very deep into the metal.

And in fact, would come to see as the mechanism, when we talk about the mechanism of pitting would see that pitting stops when the entire material perforates through that particular pit. And sometimes pit dimension is so narrow from the width part of it, not the depth part of it, it is very difficult to recognize.

And interestingly some of the times that pitting at the pit rust forms, and that rust might be colorless, or so that time that might cover up the pit, and that covering of the pit might lead to another confusion that whether there is a pit or not.

So, there are many issues with the pit. And its basically a very sometime it becomes very confusing that whether it is a pit or not. For example, sometimes you have a rust layer, even in case of steel rust recognization is bit easy because the rust color is absolutely different. It becomes a kind of brownish color rust. Sometime it become little darkish, but mostly it is brownish because of the ferric oxide.

Now, that brownish rust can cover up the entire surface, and if you remove the rust, you might see that there would be some sort of pits. And if you do cross sectional analysis, let us say you somehow expect that the pitting has formed. So, you can do cross section and see under the microscope. You might see that the pit has grown quite deep inside the material. So, that becomes very difficult whether the pit has formed or not.

Of course, there is a technique which is called cyclic polarization that might give you that whether the pit has formed or not, from the understanding of potential called E pit. We call it potential corresponding to pitting. But the best way to recognize that whether the pit has at all formed, even if it is a meta stable pit by the ERP which is called, I will talk about that ERP is basically the repassivation potential, fine.

So, that ERP can tell you that below that if you can maintain that potential below that particular ERP potential the pit formation would be very very minimized, can be very minimized. But, if the potential goes beyond ERP, there could be possibility of meta stable pit.

What do I mean by meta stable pit? That some pit can form and then again re recover, ok, from pitting. That can only happen in case of standard in case of passivating metal. So, that during passivation meta stable pit forms; that means, at a locally some passive layer has got damaged and then the pit initiates there but because of the strong passivating nature that pit can again cover up, ok or can recover from pitting.

So, that particular tendency is visible till it reaches to the potential corresponding to E pit which is potential corresponding to pitting, then only the pit starts growing, ok. So, that pit would not get recovered, ok, would not be would not cover up or would not the passive layer cannot cover up that pit, the pit will continue to grow, ok.

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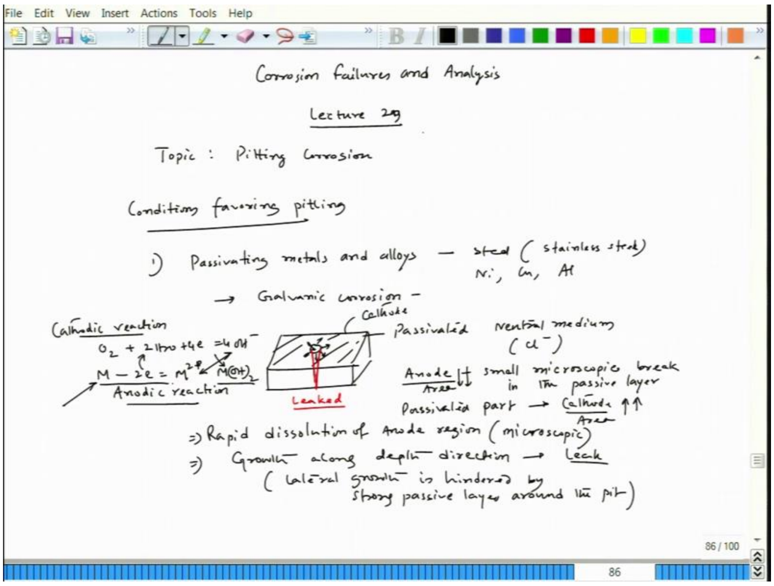

Corrosion failures and Analysis

Lecture 29

Topic : Pitting Corrosion

Conditions favoring pitting

i) Passivating metals and alloys — steel (stainless steel)
Ni, Cu, Al

→ Galvanic corrosion –

Cathodic reaction
$O_2 + 2H_2O + 4e = 4OH^-$
$M - 2e = M^{2+}$ $M(OH)_2$
Anodic reaction

Cathode
Passivated
Leaked

Neutral medium
(Cl^-)

$\frac{\text{Anode}}{\text{Area}}\downarrow\downarrow$ small microscopic break in the passive layer

Passivated part → $\frac{\text{Cathode}}{\text{Area}}\uparrow\uparrow$

⇒ Rapid dissolution of Anode region (microscopic)

⇒ Growth along depth direction → Leak
(lateral growth is hindered by strong passive layer around the pit)

So, those kind of things will start analyzing. So, the course is, and lecture 29, and topic Pitting Corrosion, right. Now, first of all let us see some of the conditions which would favor pitting. First is of course, passivating metals and alloys, like steel, and in the steel if we want to specifically mention then stainless steel, fine, then nickel, copper, aluminium. So, those are the cases where we can expect passivation and pitting can happen.

Now, and if pitting forms, pit forms in case of passivating metal, and if the metal is in the passive state, it can be serious, it can grow quickly. For example, why it also involves little bit of galvanic corrosion, fine. So, let us see. For example, let us say this is a surface and this surface is already passivated, fine. Now, by some means there is a small segment where the passive layer is broken. So, now, that passive, and let us say it is in neutral medium. And of course, there are some sort of chlorine ion present.

Now, if that small part gets broken then that small part becomes anode, and you can mention small microscopically microscopic brick in the passive layer. Now, rest of the part which is passivated which is cathode which would become cathode and so, that cathode area if you see, so if you compare the area of this one and area of this one, so this small segment is the anode and rest of all the area is cathode, fine.

So, it becomes a favorable area consideration for rapid corrosion of that anode area, ok. So, this, so the cathode area is very very large, anode area is very very small, if you compare the area factor area of both the regions. So, that leads to rapid dissolution of anode portion. And remember this is microscopic, this is microscopic.

Interestingly, when it happen, because this actually galvanic corrosion takes part and let us say if oxygen is there; that means, dissolved oxygen is there, and if it is a neutral media, so this is the cathodic reaction. And let us say if it is some metal M minus 2e equal to M2 plus, this is anodic reaction, fine. So, these are the two reactions.

Now, interestingly that might lead to a kind of rust which is M OH whole 2. So, this is the rust that can form due to the reaction between the cathodic product, cathodic reaction product and anodic reaction product. And so, this rust because surrounding area is passivated that rust may not spread, that may not spread from the region of anode, ok.

And if that cannot spread and at the same time the entire metal surface provides the area for cathodic reaction, so to meet the electron requirement for cathodic reaction, so this reaction has to happen quite large number because this electron will be provided to this, this particular reaction. So, and the rust is not able to spread out. So, that means, corrosion will be concentrated in that small microscopic area.

And corrosion means dissolution or metal dissolution. So, that means, this reaction has to happen in a depth direction rather than in the lateral direction because it cannot spread, because surrounding area is covered with a very strong passivated layer. And that also provides area large area for cathodic reactions. To meet that electron requirement the depth in the depth direction it should grow.

So, this particular growth will happen in the depth direction. And at some point of time, this will go till to the end of the bottom surface and then it becomes leaked or perforated, fine. So, that means, finally, it is a growth along the depth direction and final part is leak or perforation, ok. Because why? Because lateral growth is hindered by strong passive layer around that particular pit, around the pit.

So, now you could realize that if that particular small pit is macroscope microscopic, it will be very difficult to observe through naked eye. So, that means, you could see that here also galvanic corrosion comes into picture, because that is basically the galvanic corrosion is the start or the initiation of you can say, you can say the initiation of pit, ok.

Of course, to start where that particular pit will start that will be decided by many other factors, ok. But corrosion start will be decided by the galvanic corrosion, ok. So, now this is first part which is a passivating metal.

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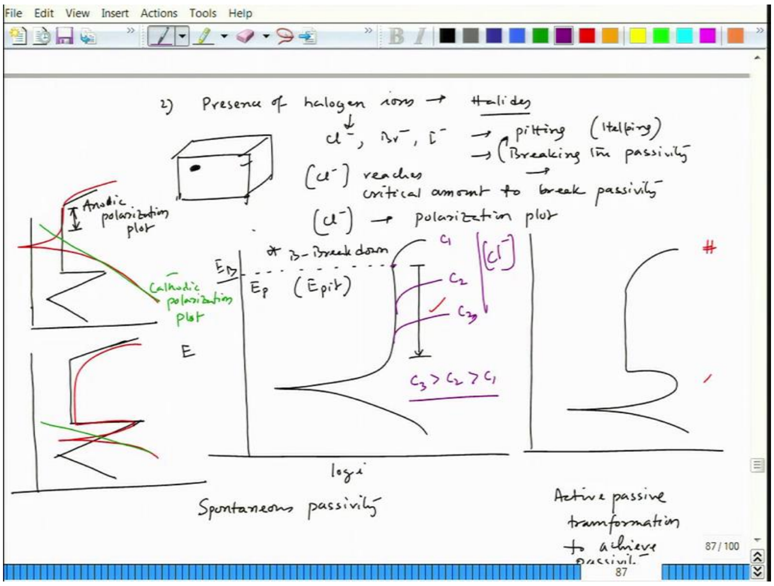

Second one is presence of halogen ions or presence of halides, ok. So, this halogens ions are nothing, but chloride, bromide, iodide. So, these are the ions which can lead to pitting. In fact, these elements are actually helpful in breaking the passivity. It acts negative or opposite to passivity or it actually hinders passivity. So, that is what that will help passive. So, this is helping pitting and this one also helps to start pitting.

For example, on a surface, let us say this is a surface. So, let us say this is the surface it is exposed to the chloride ion, let us say at some point of time chloride concentration goes up at some location, ok. And let us say that chloride ion concentration, chloride ion concentration reaches critical amount to break passivity, ok. So, once that passivity is broken, so this is the same as the situation what we have explained here, ok. So, that particular part will create a small bit, ok. So, that means, and of course, there is a every halogen ions, halogen ion has got a for example, chloride, bromide or iodide. So, they have they must have they must be around that the presence of that chloride ion should be a critical amount that will initiate pitting, ok. So, we will talk about this presence of chloride ion on polarization plot, ok.

So, now, if we try to look at passivity, for example, if I try to look at polarization drag diagram for passivity, let us say this is E, this is log i. The polarization plot of for a passivity two different kinds of passivity can be observed, one is spontaneous passivity. So, like this, one is this, another could be like this. So, like this. So, this is spontaneously passivating or you can say spontaneous passivity. And this is active passive, active passive transformation to achieve passivity, fine.

Now, if you go back to mix potential theory, you would come to know that how this diagrams arrive at, ok. It is all based on interaction between cathodic and anodic lines. So, for example, if I try to see that this part, so now, you have cathodic, anodic line is this, let us say, this is the anodic line, and the cathodic line, let us say this one is the cathodic line, ok.

So, this is cathodic polarization line, and this is anodic polarization line, fine. Let us say this is the potential. So, now, if I try to look at the polarization plot, if you do, if you do make a polarization plot with the help of potential stat, so now the plot will be looking like this, plot will be like this. If you see this, this is the plot, ok.

Similarly, in this case, in this case, if you want to see the why such kind of plot has arrived at; if this is my anodic plot, this is anodic polarization plot line plot or instead of line I can say plot this is plot, ok. So, this is anodic cathodic anodic line, the black one, this is the anodic line. And the cathodic line if I try to see, so cathodic line will cut here. So, this is the cathodic line cathodic plot.

So, now, if I try to see the plot nature, it will be look like, it will look like this. So, you see this is exactly like this. So, this is the interaction between cathodic and anodic plots while considering mixed potential theory, and you can get achieve this kind of lines.

Now, this point, where sharp break happens in the passive region. So, you can see that this is the passive region here also. So, this is the part where the passive film has grown, ok. As you increase the potential passive film actually grows. And then pit starts, and that pit starts to grow because of the strong passivity, the whatever pit forms, small small pit forms that will get recovered, that will recover because of the strong passivity of the metal or that could be filled up, fine.

But, at some critical potential, the passivity will not be able to cover up that pit. So, the pit starts growing. So, this is the point which is call Ep or we can say Epit, ok. And you can also say sometimes this is E break, E_B or E breakdown, B means breakdown. Remember there is, that particular point might happen without breakdown even if it reaches to the point where oxidation, oxygen reduction starts, ok.

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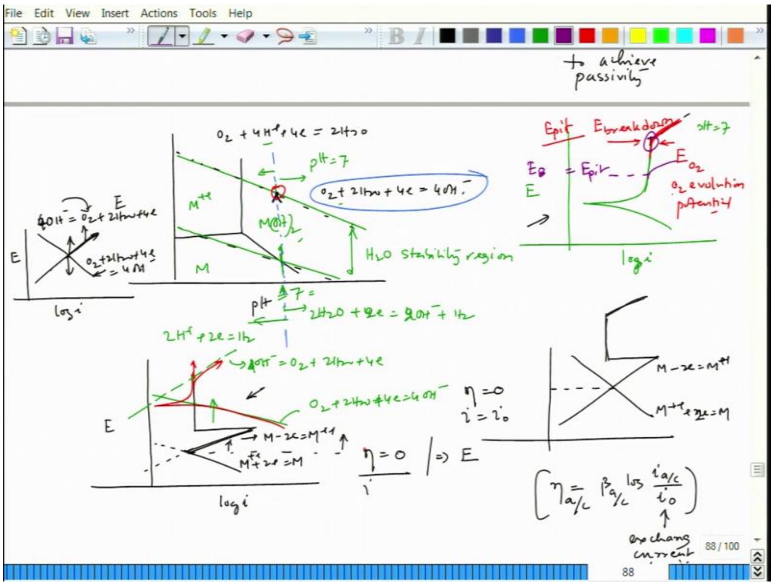

So, if you go back for example, if I try to look at some pourbaix diagram, let us say this is the pourbaix diagram I am looking at. This is the pourbaix diagram I am looking at. Let us say this is the oxygen line. This is the hydrogen line. You know you recall potential versus pH, oxygen line means we have two reaction O2 plus 4 H plus plus 4e equal to 4, $2H_2O$, and then another reaction can happen plus $2H_2O$ plus 4 e equal to 4 OH minus.

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

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

$$\eta_{a/c} = \beta_{a/c} log\frac{i_{a/c}}{i_o}$$

And in case of hydrogen line, so let me draw the hydrogen both the line like this in blue color, green color. So, these are the two lines, and between these two regions we call a water stability region in pourbaix diagram. And let us say this is M, this is M plus plus, this is Mn M OH whole 2. So, let us say there is a passive cell.

Now, this reaction happens beyond pH 7 and this reaction happens below pH 7. So, there are two other reactions also. For example, below this pH which is acidic in nature H plus 2 equal to H_2. This reaction happens. Beyond this we have another reaction which is called water reduction. This reaction happens.

So, if I try to polarize at this pH, for example, let me take this pH 7, fine, pH equal to 7 let us say, I try to polarize. Now, at some point of time the polarization because it is entering into passive region, the polarization point, polarization line can, this is E log i, i is current density, so polarization lines can look like this, ok.

And if it is a cell spontaneous passivating, so it can look like this because it is entering into and the pH is 7; because it is entering into as you increase the potential it is entering into M OH whole 2 which is a passive layer forming on top of metal surface. So, it will passivate.

Now, if that particular passivating metal is very strong; that means, the passivation is very strong, the film may not break, film there could be pit formation, but the pit will cover, will get covered up because of the strong passivity, above which will cover up the pit, pit will not grow.

But once it reaches to this potential, so at this pH, so it will reach to this potential. So, this is the line I am doing by polarization this blue line, ok. So, now if you reach to this potential, from this potential as you go up this reaction starts taking care taking over ah with respect to the polarization line.

For example, if I try to do a mixed potential plot, ok; so, let us say, ok; so, let us say this is the polarization, this is the anodic plot for anodic plot E versus log i, anodic plot only, ok. So, that means, this part, from this part onwards, this side is m minus plus 2 e M, this side is M minus 2 e equal to M plus 2. So, this if you go beyond this particular ah voltage which is corrosion potential, so this is basically the corrosion potential.

Now, if the cathodic line comes like this, cathodic polarization line, so then your plot would be, ok, fine. So, ah sorry this is not corrosion potential. This is called, this is with respect to the single electrode metal system, this particular line could be over voltage equal to 0, ok.

So, some potential, corresponding to some potential which is related to over voltage 0, because if I try to look at a cathodic and anodic reactions, so this is M plus plus plus n e equal to M of 2 e and this is M minus 2 e equal to M plus plus. So, this is anodic line, polarization line which is coming from what over voltage equal to anodic over voltage and cathodic over voltage beta ac log i, i0.

This is the Tafel equation, we are using to plot these two lines, ok. Now, a means anodic c means cathodic. So, if you take a that time you take all those current values a, and this is the exchange current density, this is exchange current density, exchange current density.

Now, so that time this particular point corresponds to over voltage 0 and i equal to i naught so; that means, this point corresponds to because this is nothing, but if you extend this, so these are the 2 lines, ok. So, like this. So, now, if you try to extend this line which is basically the theory of passivation that polarization part of the anode, it will at some point of time it will start bending backward and then go upward, and then at some point of time it will break. It will just go like this.

So, this breaking can happen due to pitting, at the same time this can happen due to oxygen reduction process or oxygen evolution process. So, now, if you try to see this reaction, this reaction also has 2 parts. So, this reaction also has 2 parts. So, if I try to look at oxygen evolution reaction. So, this is this 2 parts log I can be done. This is O_2 plus $2H_2O$ plus 4e equal to 4 OH minus, and this is this reaction, and this line would be reverse line 2 OH, 4 OH minus equal to O_2 plus $2H_2O$ plus 4 e, ok.

So, now, if we go towards this, towards this, potential if I go towards this this oxygen evolution starts, if I go downwards oxygen reduction starts. So, that means, that oxygen evolution reaction would happen. Now, as we see that once the potential is reached to this level because this is going like this perfectly fine, because it has entered into the M OH 2 region at that pH 7. Now, if I try to see because this particular plot and this plot are corresponding each other. Now, this green line is basically the oxygen reduction line oxygen reduction line, ok.

Now, it has also has its own oxygen evolution line, fine, because at some point because we are going towards this positive potential. Once this particular line, this red line come across this green anodic polarization plot for oxygen evolution reaction, then immediately if the if there is no pitting, because the polarization the passivation is very strong, if there is no pitting, then instead of going upward like this it will take a turn like this, ok. So, the curve will look like this fine, ok.

So, now, this point that time is not E breakdown or E pit, ok. So, they can be synonymous at some time. But sometimes they are not, they are different, ok. But now, it is not it is not a breakdown because this is basically, I can term it as E oxygen line or oxygen evolution line. This is oxygen evolution potential; we can say this. So, this is not break.

Now, that pitting happens many a times it does not, without reaching to that particular potential pitting can happen before that. So, that time this can go like this. So, that time we can say that this is E pit or sometimes we can say this E breakdown, E B, ok.

So, that means, this is the basic difference between oxygen evolution and E pit. Many a times you have to look for that particular potential. And if that potential matches with the pourbaix diagram or that particular metal, at that p H, you can be assured that that is oxygen evolution line, ok. So, you have to be very careful in deciding the E pit. Sometime it confuses with the oxygen evolution potential.

So, now, coming back to this, chlorine effect, chloride effect. So, now let us say this is the pitting breakdown potential or E pit. Now, if we increase the chloride ion that E pit can happen much earlier, and if you increase further, it can happen like this. So, that means, let us say this is chloride ion concentration one C, C1, this is C2, this is C3.

Now, you can say that this is chloride ion concentration. Now, we can say that C3 is greater than C2 is greater than C1. So, that means, if you increase chloride ion concentration, the pit formation tendency also goes up, ok for a particular passivating metal. So, that is what this presence of halogens ion, halogen ions are very is very very dangerous to the passivating metal because it breaks at some local point and it starts creating all sort of heat related problem to the material, ok.

So, let me stop here. We will continue our discussion on pitting in our next lecture also. We will try to understand mechanism of pitting, and then once we know mechanism of pitting, we can somehow construct some of the protection routes which can prevent pitting. Let me stop here.

Thank you.