Corrosion - Part I Prof. Kallol Mondal Department of Materials Science Engineering Indian Institute of Technology, Kanpur

Lecture – 05 Crevice and Pitting Corrosion

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Hello everyone. Today, we have our 5th lecture. And in our last lecture, we started talking on different forms of corrosion. And we completed uniform corrosion. And then we started Galvanic corrosion. And we will continue with the galvanic corrosion, some more information or a knowledge on galvanic corrosion. We talked about distance effect, we talked about polarity effect that means, if we are trying to have a kind of protection of steel by zinc, then zinc is active and iron is noble.

And that is what iron acts as cathode, where cathodic reaction takes place. And zinc of course acts as anode and where anodic reaction takes place. But, we have seen a kind of situation, where the temperature goes beyond 60 degree Celsius; then zinc converts to zinc oxide due to the reaction with the species that are forming due to corrosion.

And this zinc oxide then acts as cathode, because zinc oxide position of zinc oxide in the galvanic series is evoke iron. So, iron would then act as active component. So, iron dissolution would happen, and zinc cathodic reaction would take place on zinc oxide

surface. So, we have to be careful while taking some metal for sacrificial protection just like in case of iron and zinc.

Now, we also looked at a brief description of galvanic series. And we thought that we would know better on this galvanic series, when we talk about electrochemical series that will come little later. Now, in the galvanic corrosion, we have one more important issue, which is area factor.

In case of area factor this is a very interesting aspect. For example, if you have two copper plates and if you are trying to join them or rivet them with steel rivet. This is made of iron and this is copper. This is a situation.

And when we have steel plates, now let us say this is iron plates, which are reverted by brass. And the brass is nothing but copper zinc alloy, where copper is predominately high. In these two cases, if we dip this two riveted object in HCl solution 3.5 percent in HCl solution, we would see that in case of iron revert joining two copper plates would lose would lose its strength quickly as compared to the brass rivet, which are fastening two iron plates. And this there also the galvanic effect is active, in fact what happens in case of this iron corrodes quickly, since, iron is active as compared to the copper plate. And then, it the joint becomes lose.

And in this case, cathodic reaction happens on copper surface. And since it is a kind of neutral solution if we have dissolved oxygen, then the cathodic reaction, which will take place on copper surface would be oxygen plus 2 H2O plus 4e equal to 4OH minus. And since iron is corroding, so iron minus 2e anodic reaction would take place plus. So, this is anodic reaction and it acts as anode.

Now, if we see the number of cathodic reactions that are taking place on copper surface, since copper surface has got a huge area compared to the iron rivet surface. So, the total number of cathodic reaction on the copper surface would be hugely, it is very large.

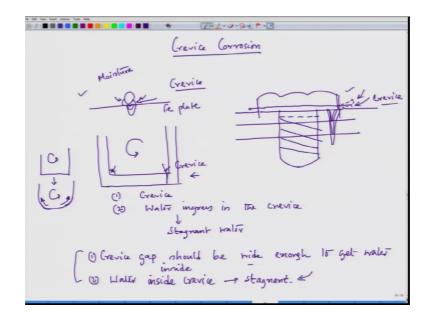
And in order to supply the amount of electrons for this cathodic reaction, iron has to dissolve quickly, because this electron would be supplied from this anodic reaction. Rate of iron dissolution would be faster. And this is the concept of area factor in galvanic corrosion.

So, the cathode area if cathode area is very large and anode area is small then the danger of galvanic corrosion is very aggressively felt, just like this case. But, in this case it would also lose, but the loosening would be a little this time to time for this loosening effect would take place would be higher time, the longer time, the duration would be longer, because here the brass is cathode and iron of course it will be anode.

Now, cathodic reaction would take place the same reaction would take place on the cathode surface, which is basically the brass surface. And iron dissolution would take place on the anode surface. And since the cathodic area is small, the number of cathodic reactions would be small of course. So, in order to supply the electrons for cathodic reaction, the total amount of iron dissolution would be less as compared to this situation. So, the loosening effect would be hindered.

So, now from this idea, it is very clear that in order to design some joining material, we have to make sure that the cathodic area should be small as compared to the and anodic area should be large, so that case the galvanic effect would be felt less severely.

So, this is very important factor. And we would talk about this area effect, when we talk about inter granular corrosion, there are also the area effect would be severely effect. Now, once this particular galvanic corrosion again will touch upon, when I complete explanation on, mix potential theory.



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Now, let us go to another form of corrosion, which is called crevice corrosion. Now, when we talk about crevice corrosion, we have to understand what is crevice. Now, if we have a plate surface on this, if we have a small dot particle, this is the small dot particle and this is let us say iron plate. And this particular surface, if we have moisture, now of course these particular region, these two region there could be possibility of water ingress and these water ingress could be possible, if this opening is wide enough, so that the water can take over the surface tension resistance to get into this particular sections. So, this is a small region, so this region is a small gap, where moisture can sit or moisture can enter. And interestingly in this gap, moisture once moisture goes in, still moisture remains stationary or stagnant. And this is a particular example of crevice, this is also crevice.

Another example of crevice is let us say, I have a bolt and this bolt is joining two plates. And two plates these are joining, these are the threads. Now, when we have this bolt, we also sometime put a rubber gasket, rubber small rubber thin, thin rubber a kind of sheet, which will act as the gasket.

Now, this gasket what is the reason for this gasket, it will tighten it. Of course, one is it will not allow this particular bolt to be loose. But interestingly, if this gasket is little wide, then this gasket end could have this kind of appearance. And once, we have this gasket appearance like this then it is also forming a crevice.

And in that section again water can sip in, and it will remain stagnant there. This is another crevice region. There could be formation of crevice in case of corners, for example, in the metal corners like this. If this is a small metal tank, now this corner is also acting like a crevice.

Here also, even if there is turbulent, turbulence in the water in the water storage turbulence, but this corner region will be nearly stagnant. So, this is also crevice. Now, we have been talking about two things. One is crevice, and second is water ingress in the crevice.

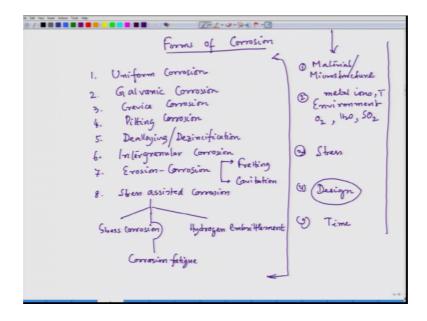
When we talk about water ingress, we also talk about another thing, which is called stagnant water that means, this gap should be this crevice gap should be wide enough should be wide enough to get water inside. And second is this water inside crevice should be stagnant.

When we have these two situation met, then the corrosion in the crevice region is extremely high, that the rate at which the dissolution takes place in that region would be so high, that the surrounding region might look very clean, but that region there could be possibility of corrosion towards the depth direction, that means, in this case there could be a small gap that is forming.

And that gap can that corrosion point can ingress towards the depth direction. So, if this is my thickness of that wall at times, this wall can be punctured. And there could be leakage. And this is the level of crevice corrosion that is possible. Here also there could be possibility of crevice corrosion around this region.

So, the corrosion would be so fast, that even without giving any signature, it might leak the container. Here also, since there is a crevice pole crevice and water moisture content is there also this is stagnant. Here also the corrosion can take place, and then corrosion attack can be like this. So, these are some of the deadly corrosion effects of crevice.

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And we have to make sure. And now as we have mentioned in the on the slides, if I go back to that particular slide, if you see that on the right side, on the right side we have a factor called design. Now, when we talk about electrochemical nature of corrosion the design does not come into picture, because the electrochemistry does not talk about design. It talks about the rate at which anodic and cathodic reactions are going on. So, now when we talk about crevice, then the design factor would come very handy in order to control this crevice attack. For example, in this case if we have a dirt content on the bottom of steel container, it is always better to get rid of those dirt's, that is what water container time to time it is better to go for cleaning. And the cleaning would allow this dirt particles to get rid off and finally that will reduce the crevice attack.

For example, in this case this is a typical case, where we can have a design criteria which will control the crevice. Now, when we control this crevice, that time we have to make sure that the gap should increase, so that water would enter.

But when there is a flow relative flow between the water and the container then if we increase this gap that would allow turbulence to take place. And that turbulence would not maintain this stagnancy, because during crevice this stagnancy is very important issue. If we have stagnant solution in the crevice, then only crevice attack is possible very at a very high rate. So, if we have to take care of this stagnancy also, so that the turbulence should be felt of course. Turbulence should not be, so high that it would lead to another kind of corrosion, which is called erosion corrosion.

So, now we have to have a wider gap in the crevice region, even if we are not able to remove the crevice, then we have to increase the gap, and to the allow this stagnancy to break this stagnancy by introducing turbulence in the water. Now, in this case this exactly can be done. So, now, instead of having a sharp corner, we can have kind of container design like this. So, once we have a container design like this you see in this portion I have avoided crevice. And now, if there is a flow in the water, so this flow in the water is actually does not allow this stagnant solution to form in that region. So, this is a typical example how we can improve design, so that we can avoid some deadliest forms of forms of corrosion.

And in this case for example, we have to first try that there should not be any crevice. So, one way is we can chop of these particular edges, which will allow this gasket not to protrude out, so that the crevice is avoided. So, this is the design factor we can take it think of. So, now this crevice corrosion itself is a wide subject. So, we are just giving some sort of nutshell that what is the form of crevice corrosion.

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Now, the next form is a before going into the next form I just would like to show some of those common crevice attack that is possible. Now I have just giving one particular a rod. This rod is very common is not it. You have seen all those in on the road itself, if you see that this particular things are available, while construction is going on. This is nothing but a reinforced bar. And this is also a ribbed bar, if you see this are ribbed, this ribs are formed, because it will hold the cement better than the plain bar.

Now, if we see this, if we concentrate on this particular section, if I see from this; so, if I see a kind of route of this particular rib, I am talking about the route of the rib, you will see that the route of the rib has bit more red rust compared to the other portion the flat portion. See you see this, this is the route, and in this route you have bit more red rust than this flat regions, ok.

Now, let us take another example. For example, here if you see this, if you see this, the route is having more red rust compared to the base regions ok. Now why does it happen? Now if we see this, this is lying on the floor and rains are falling on this. Now, ones there is a dry weather just after the rain from everywhere the water would be evaporated.

But, in the this is for me a kind of crevice the small crevice if you see this, small crevice it is forming just at the root of at the base of this particular rib. And there water can deposit and it would stay this is stagnant absolutely stacked and lock soluble water, and that would go for a higher corrosion. So, that is what you are getting more red rust at the

route of this particular ribs other portions are relatively a red rust free ok. So, this is one typical example that where you can see crevice corrosion.

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Now, let us go to the fourth mode of corrosion. This is also a very deadly form of corrosion, which is called pitting. The criteria for formation of crevice corrosion is almost similar in case of pitting. In case of pitting also we need stagnant, solution, and on the surface. If water is flowing, if the water is stagnant, and if the metal, there are some sort of weak regions. I mean to say that weak region means some of the active regions like grain boundary. Grain boundary is a place, where the activity of that region is more than the activity of the grain body.

Here, I am talking about electrochemical activity, so that regions if we place that particular grain for example, if we have a microstructure like this. Now, the grain boundaries after reaching we see the grain boundaries can be seen. And these grain boundaries can be seen, because the grain boundaries are attacked more in the etchant because the grain boundary is a very active region. So that means, grain boundary potential if we compare the reduction potential of grain boundary, and grain body, the grain body has a positive reduction potential as compared to the grain boundary potential. So, that is why the grain boundary region acts as a anode, so it dissolves more.

So, if we have weak places like this for example, another weak place where this the on the metal surface the weak place is for example, iron. If it contains inclusions or aluminium alloys, it can contain inclusions or magnesium alloys, it can contain inclusions, those interface between inclusion and the matrix is another weak place. So, those are the regions where pitting can initiate. So, the initiation of pit happens on weak and active region of a metal.

And also crevice is another region where pitting can initiate. Now, once pit forms let us say a kind of small pit forms on the surface, if we see this cross section wise, let us say this spit forms as a small dot. But interestingly this pit may not grow like this it may not grow like this. But interestingly pit growth can take place very rapidly, if we see the depth wise very rapidly like this. And this pitting can be, so rapid that it can puncture a plate steel plate, and for that stagnant solution is one of the criteria's.

So, the mechanism of pitting and mechanism of crevice they are nearly similar. But we are not going to discuss all those mechanism. But I am just saying that what is the form? So this is the kind of form. For example, if we have a plate like this. So, this plates you have the small dots. And these dots are nothing but pits. And around that dots you will find little bit of red rust in case of iron and many a times it punchers the plate ok. And why I am telling stagnant solution? Let us say, if we have a water and this is the metal surface, if we have water flow, if the water flow is, less, the number of pits and the depth of pits will be less, will be more it is just reverse and if there is a water flow then the pit formation would be hindered.

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Now, as we have mentioning that the pit can be so dangerous. I just would like to give you one example. This is the plate. Let us look at this plate and this plate the material is 304 stainless steel and when we see this 304 stainless steel, we have a kind of idea that stainless steel means it should be stainless that means, the corrosion would be minimized.

And in fact, if you see this is a very old plate almost about 3 year old plate and this was used for accelerated corrosion test of concrete rivers that means, this was dipped in the solution and this was acting like a anode, anode material. Now, when we use this, after sometime we could see that this is developing kind of small small holes.

And if we see this holes, if I would like you to look at this particular plate, if we see this hole, I have just put little bit of light on the back of this particular plate. You can see that gaps are there. And it these are looking like stars blinking; is not it? And this small small holes, we have not formed. In the beginning, it was a flat plate without any small small gaps, small small holes.

These holes are formed after use of this particular plate as an electrode in the electrolyte, which contains NaCl and FeCl3. Now, these are called pits. So, now this is a rarely thick plate, which is almost about 3 millimetre plate and 304 stainless steel. Around that pit over all this is quite shiny, considering the fact that 3 years have spent. This particular plate has spent 3 years in open atmosphere we have not protected it, but this pits are formed. And this pits are so aggressive, that it has punctured this plates.

So, I am just talking about a kind of a structure which is made of some kind of material like this. And this pits and then these structures are designed to hold some load. Now, once we have load hole like this the cross section is decreasing. Now, the design stress would be design load will be felt heavily on this smaller cross sections and then the stress should go beyond yield point and then it will start yielding. And it may arise the situation may arise that it will crumble into pieces, so that is what this pitting corrosion is so dangerous that, it will not give you any signal before a fracture happens.

And though we are able to see, if we see though we are able to see these big holes, sometimes, this holes are so microscopic, until unless you go under the microscope, you will not be able to see it, but actually it is it has punctured. And now it has reduced the cross section thickness. So, this is a kind of a severe mode of corrosion form, when we

talk about 8 forms of corrosion. So, let us stop for this lecture. And then, we will continue this subject in our 6th lecture.

Thank you.