Corrosion - Part I
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Lecture – 03
Types and Forms of Corrosion

Hello everyone. Let us start our third lecture. As we have discussed in our first two lectures on importance of studying corrosion, we have also given some examples, some of the catastrophe, we have also mentioned. And finally, as we go ahead and then we have seen that corrosion involves four parts and it also is directly associated with electrochemistry. And the four parts are two electrodes which is; one is cathode, one is anode. We have electrolyte, where ions will be flowing; and then we have conductor where electron will be flowing. And then, we have a complete circuit and then corrosion will go on. So, a corrosion is electrochemical in nature, that is what we have understood.

And we have also given two examples; one is zinc corrosion in dilute acid where on the zinc plate, you have hydrogen bubble and this hydrogen bubble is forming due to cathodic reaction which is hydrogen plus and takes one electron and it converts to hydrogen atom and then finally, two atoms joined together and forms hydrogen gas. And that reaction happens on zinc surface itself. And this particular electron is coming from formation of ions, formation of ions of zinc which goes into solution from the metal part and that electron will be released into the metal. And then metal acts as a conductor and that electron comes to the place where hydrogen evolution reaction happens. So, that way the complete circuit is, the circuit is complete and this zinc actually finally, forms zinc chloride because already you have chloride in that particular HCl medium and that way zinc corrosion goes on.

We have also give an example of iron corrosion in atmosphere and if I go back and try to see that particular slide

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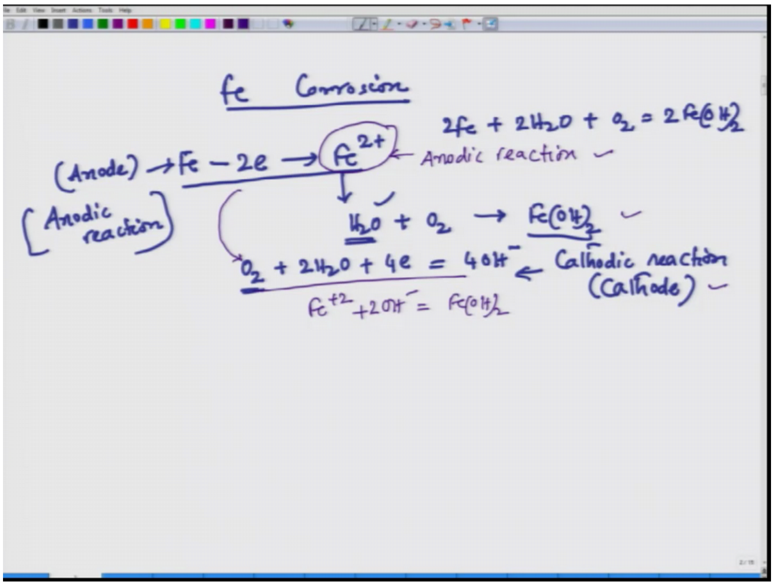

Fe Corrosion

$2Fe + 2H_2O + O_2 = 2Fe(OH)_2$

(Anode) $\rightarrow Fe - 2e \rightarrow Fe^{2+}$ ← Anodic reaction

[Anodic reaction]

$H_2O + O_2 \rightarrow Fe(OH)_2$

$O_2 + 2H_2O + 4e = 4OH^-$ ← Cathodic reaction (Cathode)

$Fe^{+2} + 2OH^- = Fe(OH)_2$

If you see that iron is actually going to iron plus 2 ion electrons are released and these electrons are taken by cathodic reaction which is oxygen plus 2 H 2 O plus 4 e equal to 4 O H minus. And here, we have seen that this particular ion reacts with this H 2 O plus O 2 and goes to F e O H whole two. In fact, this particular reaction is anodic reaction and this particular reaction is cathodic reaction which happens on the iron surface itself.

Now, this iron plus 2 reacts with O H minus and forms F e O H whole 2 which is same as this reaction. Finally, this reaction is parallely taking place. This is also electrochemical because this is anodic reaction, this is cathodic reaction. This anodic reaction happens on the iron surface iron corrodes and cathodic reaction also happens on the iron surface which takes care of that electron which are released by iron while formation of ions. This is also electrochemistry.

Now, we will get to the thermodynamics of these reactions as well as how we can explain this formation of ions at different levels of pH. And, we would basically consider aqueous corrosion. Now, since I have mentioned aqueous corrosion, this corrosion can be divided into two parts; one is wet corrosion and another one is dry corrosion. Now, you must be wondering what is dry corrosion if we recall that we have mentioned that oxidation is also a corrosion process. Now, whenever we talk about corrosion process, we have to take, we have to see that whether this four parts of electrode that particular cell corrosion cell is are being satisfied.

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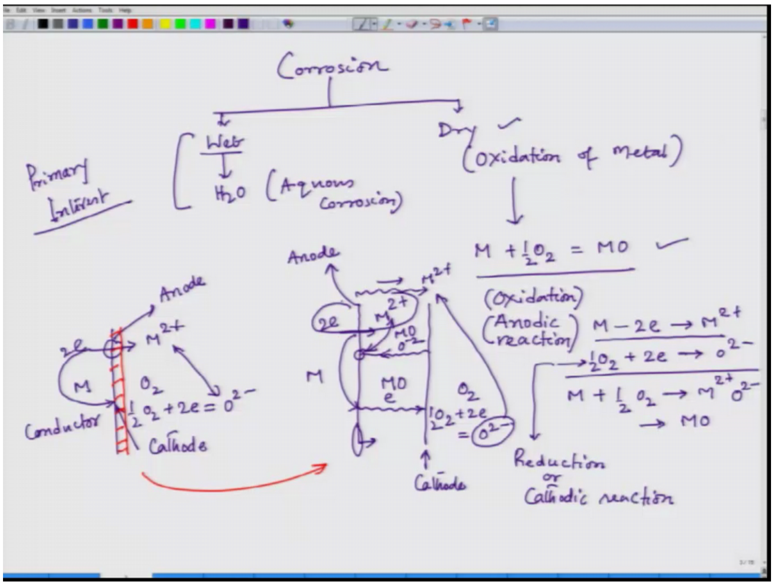

Now, let us get to as we have mentioned that corrosion can be wet and dry, wet and dry corrosion. Now, in the wet corrosion, we see that where H 2 O is involved. We also call it aqueous corrosion. And in case of dry corrosion, we are mentioning that oxidation, oxidation of metal we are mentioning that this is also a corrosion. That means, it is also electrochemical, aqueous corrosion from those two examples, it is very clear, it involves oxygen, it involves water because in one case we are dipping zinc metal into dilute H Cl solution which is aqueous solution of H Cl. And in second case, we are seeing that corrosion of iron object in the environment in the atmosphere where we have moisture which is again water; of course, there oxygen is also involved.

But in case of dry corrosion, let us just have a look at what happens at the interface of metal when oxygen is involved because anyhow I am talking about oxidation of metal. If we consider this particular reaction, O 2 equal to half O 2 M O, if I consider this oxidation reaction, let us have a look at what happens at the interface.

This is metal surface. Let us say some oxide has formed, M O and then this is gas medium. Now, in the beginning there was if we consider that there was nothing. So, metal surface we are having M going to taking leaving two electron and then forming M plus 2. And if I consider oxygen, half oxygen; that means, one oxygen atom, it takes care two electron and forming O 2 minus. Since we are having this, this notation 2 plus and 2 minus, and if they combine, you see M plus half O 2 equal to M plus 2 O sorry M 2 minus 2 plus 2 minus. This is nothing but M O which is same as this reaction.

Now, interesting, let us look at carefully this. What is this reaction? This reaction is nothing but anodic reaction, because it the metal atom is leaving two electrons, is basically red oxidation is taking place. In the sense that if we consider oxidation to be electron when metal leaves electron, we call it oxidation. Now, if I consider this reaction, this reaction is nothing but a reduction reaction, reduction or cathodic reaction and this is oxidation reaction.

Now, question is two reactions are done; now since in the beginning we have only metal surface, we have oxygen and then metal. So, if this place we have metal plus 2 formation, so two electrons are released here in the metal. So, these two electrons are flowing through that conductor and here, half oxygen takes care two electron and forming O 2 minus 2 minus, this is 2 minus. So, these two are reacting

Now, you see this part acts as anode. So, one electrode this part act as cathode; second electrode, this is conductor and here when this two reactions are this two reaction, this half cell reaction, these are called half cell reactions, this half cell reactions are taking place finally, methyl 2 plus and oxygen 2 minus they are combining and forming metal oxide. So, this metal oxide is forming on top of this metal surface. So, now, we have situation like this. So, here metal surface, metal oxide and oxygen.

Now, once we have this, now question is whether this reaction would continue or not. Now, still if I consider metal ion is forming. So, two electrons are here and these electron can go somewhere around this metal object because every metal part is basically acting as conductor. And now this electron can flow through this because metal oxide either it could be n type or p type. If it is n type, then this electronic and flow through this through the electronic area and then here can form 2 minus. Now, this ion can also move like this. Now, when it moves like this, it comes here and then combine with this and form metal oxide.

Now, if metal ion is moving on the outer side and there this particular thing can combine and form metal oxide. Now interestingly, charge flow is taking place through this; for example, here oxygen 2 minus is flowing or here metal 2 minus is flowing through this. So, charge flow is taking through this M O. So now, M O becomes my electrolyte.

And in case where oxygen ion goes through the metal oxide and reaches to the metal surface and at the interface of metal and metal oxide forms further oxide molecules are forming, that case the oxide growth is taking place on the metal-metal oxide surface. So, on the surface metal oxide growth is taking place. Now, in case metal ion is moving out from the metal, metal oxide interface and coming to the metal oxide oxygen interface and there it combines with the oxygen ion. Then the oxide growth is taking place on the surface of or at the interface of metal oxide and gaseous oxygen.

So, here also you are seeing that the condition of corrosion cell is satisfying; that means, we have cathode we have anode and in this case since this cathodic reaction is taking place at this surface at this interface, this becomes my cathode and this particular reaction is taking place at metal-metal oxide interface. This becomes my anode. An electron flow is taking place through the metal surface or it can flow through the metal oxide. So, metal oxide itself is acting as electrode, acting as a conductor as well as electrolyte, because it also allows charge flow in the form of metal ion or oxygen ion. So, this is also electrochemical reactions and here metal is oxidising. So, metal is losing in the form of oxide, this is also corrosion.

So, but here we do not have moisture. So that means it is a dry corrosion. So, that is what we have come to the condition of dry corrosion where we have oxidation. If we have time, then we would definitely look into oxidation of metal little depth, but our primary interest would be on this aqueous corrosion, primary interest. So, we will concentrate more on this in our present set up lectures.

Now, before we go detail analysis that means, when I talk about analysis, we talk about thermodynamics and kinetics of this electrochemical reactions either metal ion formation or cathodic reactions where electron is being accepted by some species. It can be ion, it can be metal again another metal or it can be another it can be oxygen. So, all those cases we would try to see their thermodynamics and kinetics.

But for the time being, we would again go back and try to see some of the forms of corrosion.

So, next topic is forms of corrosion.

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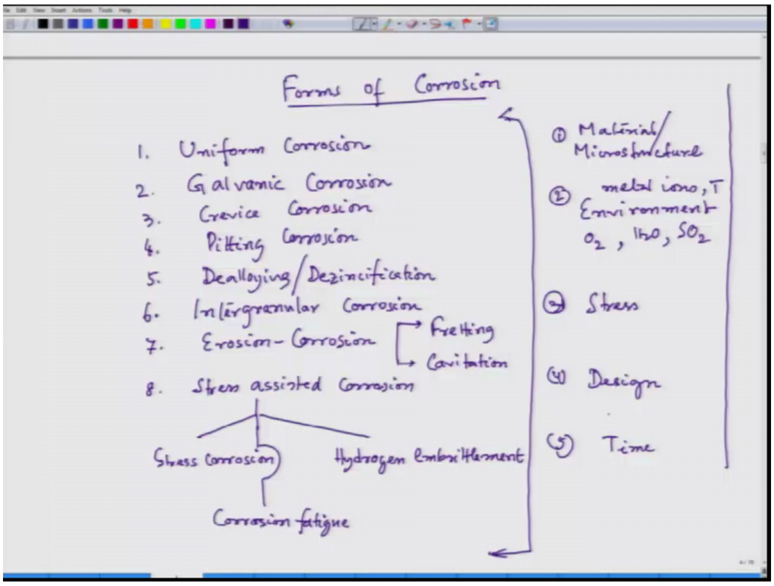

Forms of Corrosion

1. Uniform Corrosion
2. Galvanic Corrosion
3. Crevice Corrosion
4. Pitting Corrosion
5. Dealloying/Dezincification
6. Intergranular Corrosion
7. Erosion-Corrosion → Fretting, → Cavitation
8. Stress assisted Corrosion

Stress Corrosion

Corrosion fatigue

Hydrogen Embrittlement

① Material/ Microstructure

② Environment metal ions, T

O_2, H_2O, SO_2

③ Stress

④ Design

⑤ Time

For understanding these forms of corrosion I think near observation as well as a little bit of the idea what we have already learnt from this two and half lectures you can say; that means, that there would be electrochemical reaction; one is cathode, one is anode, one would be canodic reaction, one would be cathodic reactions. On that basis, we would be able to understand some of the forms means the kind of appearance I would say. So, let us look at some of the appearances and then accordingly we would define the forms of corrosion.

Now, when we come to the forms of corrosion, if we have a kind of observation rather careful observation; one form is Uniform corrosion, second form Galvanic corrosion, third Crevice, fourth Pitting, fifth Dealloying. We also call it in case of a dealloying or in case of iron brass let us say we call it Dezincification like that then we have intergranular, seventh Erosion corrosion where we have two special forms I would say two special forms one is Fretting, another one is Cavitation. And finally, we have Stress assisted corrosion where we have three segments; one is stress corrosion, then Corrosion fatigue and another one is Hydrogen embrittlement. And in case of hydrogen embrittlement, we have few other forms; for example, hydrogen blistering is one form.

And this particular definition of this definitions of different forms are basically arriving from the appearance like let us when for example, if we consider uniform corrosion as we mean by uniform means it is homogeneous uniformly happening like one example let me put up. If we see iron made sheet cover over a roof, one can find that after sometime you will have a red rust formation over the entire surface. And if it is carefully looked at add a little, carefully looked at the interface you would see that at different sections, we would have almost about similar depth of attack. I would say depth of attack means the corrosion is gradually progressing towards the depth direction of the metal surface. So, at every sections, we would have almost about similar a depth of attack. So, that time we call it uniform corrosion. So, it is a form; it is a appear, it is basically a appearance of that particular mode.

Now, for example, pitting corrosion; when we talk about pitting corrosion, we know this particular name pitting for example, on a surface as if from the appearance you would see that there is no problem, because it is has shiny as it was obtained in the as received condition when it was obtained first.

But the pitting can be extremely localized and again if we carefully look at and analyze, we would see that at some positions the depth of attack is extremely localized. And it has gone very far towards the depth direction of that metal surface, but rest of the surface looks absolutely fine.

Similarly, crevice this is also appearance. For example, let us say crevice means wherever we have a small opening in the metal structures or metal bodies and in that small opening that opening should be enough. So, that it can allow solution to go in, but the solution would remain stagnant into that particular metal opening. So, that case that would create a kind of corrosion localized corrosion, rest of the surface would look shiny, but in that localized portion, you will have red rust in case of iron I would if I consider iron surface again appearance.

Now, dealloying interestingly, if we have a brass 70, 30; 70 percent copper and 30 percent zinc and that brass if you dip it in H Cl, dilute H Cl solution after sometime we would see that the colour generally in the beginning the colour of the brass is little golden yellow. And then when you expose it to the acid after sometime you would say the surface is becoming a bit a red coloured. And if we analyze it that for example, the analysis tool is for example, A C M E D S, if we do then we would see that the copper content has gone up from 70 percent to even close to around 90 to 93 percent. So, now, at the surface that means, copper is enriching and if we look at that copper surface under the microscope, you would see that the copper surface is porous in nature.

So now here zinc where is then zinc because in the beginning it was 7 30 percent zinc. So now, zinc contain has gone down to 1 or 2 percent in that particular copper enriched region. So, the zinc has gone out in the solution and copper has been left out and that forms a particular mode of corrosion which is called dealloying. Since, zinc is going out that is what we call it dezincification. So like that, so those are basically appearance.

Now, if we try to analyze some of those all though of those variations, then we would also see some interesting part that all those variations we will see that they are decided by some factors. Generally, if we those factors we will categorise into a five major sections; one is materials definitely material and when I talk about material that means, if I consider this particular forms on a particular material, then material composition is fixed. So, that time we talk about microstructures that time we talk about microstructure, since we are fixing the composition.

Now, then we have environment, this environment is a very big thing and in nutshell we can say that when we talk about aqueous corrosion, environment the influence could be from oxygen, from moisture content, from S O 2 content or there could be possibility of presence of some metal ions; for example, Fe 3 plus ion if somewhere it is there, this F e 3 plus is not good, because Fe 3 plus allows a greater corrosion to happen in case of for example, in we have given this example zinc dipped in dilute H Cl, if we have little bit of impurity f Fe Cl 3. That means, F e plus 3 ion is there, so the corrosion rate of zinc would be much higher than in the solution where Fe Cl 3 is not there. So, thus metal ions.

Then of course, the other factors like temperature, those factors will come into picture. Then we have of course, stress, stress is important when we talk about stress assisted corrosion. One particular example we have put forth that is a silver bridge crumbling of silver bridge that people said that the reason behind that crumbling of silver bridge was a stress corrosion and corrosion fatigue.

Then, we have this is 1, this is 2, 3 then of course, we have design factor makes a huge impact. For example, if a smooth surface and rough surface smooth surface of course, it will have a less corrosion effect then the rough surface, in general.

Finally fifth it is a time. Of course, if something is exposed for longer duration of course, there will be corrosion would be more. So, these five major factors are crucial. So, in my next lecture, I would talk about this eight forms of corrosion in nutshell we will not go greater depth into it into this particular corrosion mode, because that is not our purpose our purpose is to understand the fundamentals of corrosion.

And then of course, on the way we will see that the effect of this five factors. Let us stop, we will continue in our next lecture.

Thank you.