Corrosion – Part II
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Lecture – 23
Theory of Passivation: II

Hello everyone, today will have a lecture 23 will continue our discussion on passivation. And in the last lecture, we could see that the passivation it was first experimentally shown by Michael Faraday in 1836 with the famous experiment of Iron in a HNO3 with the change in concentration of HNO3 and subsequently scratching of the iron block and then subsequent rapid corrosion.

So, when Iron is dipped in concentrated HNO3 at room temperature it passivates and then when it is taken to dilute acid there is no change, but once we scratch the iron block in the dilute acid the rapid corrosion starts. And then we also have witnessed some of the typical polarization curves, what we come across while where passivation is observed and there are 3 variants. 1 variance was like.

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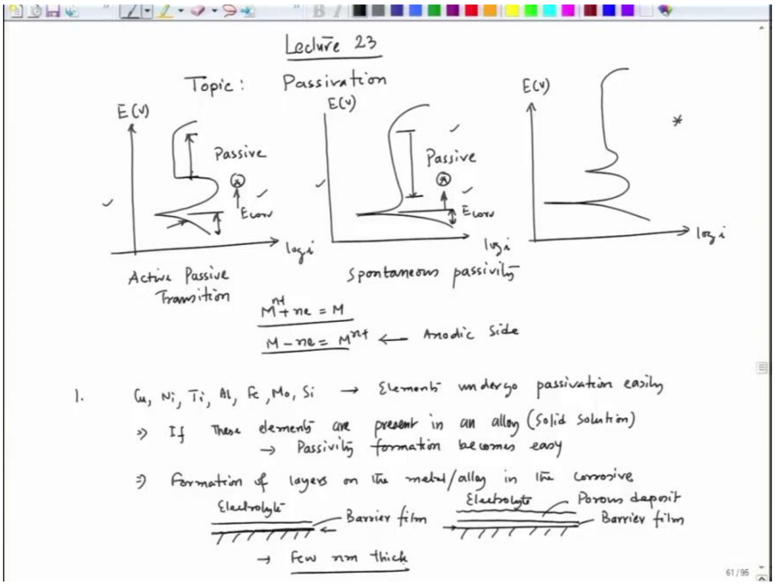

Lecture 23

Topic: Passivation

Active Passive Transition

Spontaneous passivity

$M^{n+} + ne = M$

$M - ne = M^{n+}$ ← Anodic Side

1. Cr, Ni, Ti, Al, Fe, Mo, Si → Elements undergo passivation easily

⇒ If these elements are present in an alloy (Solid solution)
→ Passivity formation becomes easy

⇒ Formation of layers on the metal/alloy in the corrosive

Electrolyte ← Barrier film

Electrolyte — Porous deposit — Barrier film

→ Few nm thick

The graph what we have plotted, 1 variance was this is E, and this is log i. 1 variance was like this and the second variance was like this and the third variance was like this. So, we also talked at this particular with a kind of a special situation we will discuss later, but these 2 cases, we could see that there is a passive region and the passive zone is up to this particular region is the passive zone.

Passive zone and out of this 2 this is spontaneous passivity. And this is Active Passive transition and almost both the cases we could see the passive region when we go into the anodic polarization side. Because, if we take this particular portion, as well as this particular portion, both the cases metal is actually depositing cathodic reaction is taking place. But if we go upward from this corrosion potential this is E corr. This is E corr corrosion potential.

We are actually going into the anodic side. So, this 2 zone we are having this reaction So, that means passivity is achieved when we go to anodic side. This we talked and then we also defined passivity is basically chemical inertness introduced into the metal when that metal is exposed to an environment due to its ennoblement or anodic polarization. There could be some other instances like lead, there ennoblement or passivation appears.

Because of the lead sulphate formation in H_2SO_4. So, those cases we have considered. Now, before we talk more about passivation, there are some characteristic features of passivation or some of the information which will be important for passivation. So, let’s state those points. 1 is some metals they show passivation like copper, nickel, titanium, aluminium then you have iron, these are the even molybdenum, even silicon.

These are the elements they provide passivation and if these are the elements undergo passivation easily. Then of course, since these elements are easy for passivation then if these elements are present in an alloy. That alloy is also susceptible or ease of passivation in those alloys become easy. So that means if these elements are present in an alloy so that alloy means in the form of solid solution.

That alloy is also can form passive alloy becomes easy. Then so when we have these alloys, then we can have a loss of chemical activity by drastic reduction. It can go into active passive mode that is this mode or it can have spontaneous passivity. Depending on whether the passive layer is already formed on the metal surface when we expose it to the environment that electrolyte or in some cases it could be nascent phase.

And then in the in that electrolyte at the passive layer forms. In case of Active Passive one example is iron exposed to concentrated HNO_3. So, there initially you will see bubbles, but after some time. You will see that the bubbles formation stops and the weight loss becomes negligible. So, that is 1 case where Active Passive transition happens. In the some of the cases you can experience this particular scenario, we will see later on.

And there are, so when we are talking about passivity, that means, it is a formation of layers, okay on the metal or alloy in the corrosive. Corrosive is nothing but the electrolyte where corrosion is highly possible and what happens in these cases. So, if this is the metal surface I can have a barrier film formation, this is barrier film or it could 1 could have a barrier film. So, this is the metal surface and alloy surface.

One can have a barrier film or layer in addition to that there could be a porous layer porous deposit in both the cases it is easily understood that the metal surface. This is the metal surface, and here it is the metal surface these are not exposed to electrolyte directly. So, here we have electrolyte. So, since the metal surface is not exposed to the electrolyte. So, the dissolution of the metal will be decided by the ion transfer or ion migration through the barrier film.

Through the barrier film and porous deposits, so, the dissolution rate drops. And another interesting part is this barrier film dimension if we consider it has been may it has been observed that these are some few nanometres thick layer forms.

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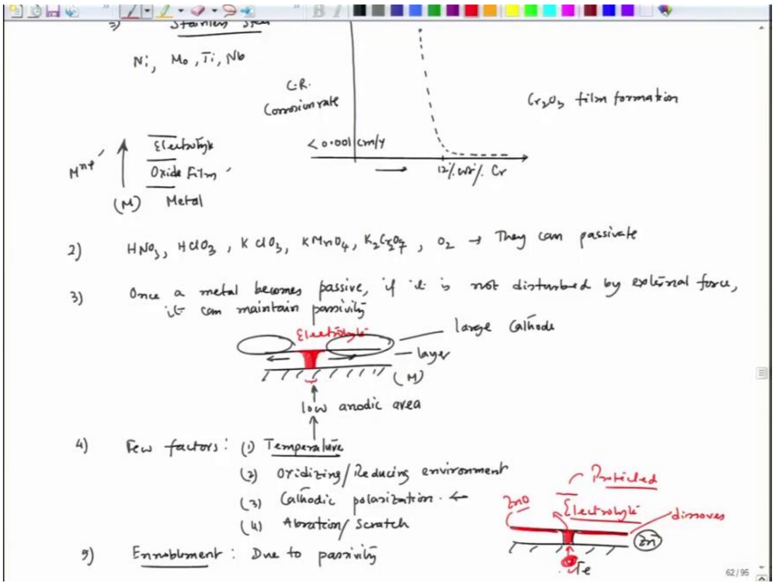

Stainless Steel

Ni, Mo, Ti, Nb

2) HNO_3, $HClO_3$, $KClO_3$, $KMnO_4$, $K_2Cr_2O_7$, O_2 → They can passivate

3) Once a metal becomes passive, if it is not disturbed by external force, it can maintain passivity

4) Few factors: (1) Temperature
(2) Oxidizing/Reducing environment
(3) Cathodic polarization ←
(4) Abrasion/Scratch

5) Ennoblement: Due to passivity

Now, coming to the other aspects. Since, we are talking about barrier film some of the elements in iron they readily forms that barrier film these particular elements when they present in the iron. For example, chromium if we talk about chromium it has been observed that in case of stainless steel, if we try to plot a corrosion rate then the CR is nothing but the corrosion rate. And that if we want to plot with reference to the weight percent chromium.

Till it reaches to around 12 weight percent the corrosion rate is pretty high and as the concentration chromium increases gradually so, the corrosion rate drops. And then it goes to very low value which can be even less than 0.001 centimetre per year. Okay. So, which is a very low corrosion rate and that happens because we have Cr_2O_3 film formation in case of aluminium it is say Al_2O_3 that forms and which passivates aluminium.

Now, the interesting part is aluminium is also considered as an element a metal which is used as a sacrificial anode. Now, as we have noticed in case of in the discussion, when you talked about sacrificial anode. So, the anode material should dissolve spontaneously. So that it provides required electrons for cathodic reaction on the cathodic surface.

Which is nothing but the iron and that is what the ion is protected from corrosion. But aluminium if it forms Al_2O_3 then it passivates. And once it passivates then it may not be anodic to the iron surface. So, that is what in case of aluminium when we use aluminium we generally add bit of other elements like zinc, so that it does not allow that passivity to appear. That means it does not allow alumina aluminium oxide.

To form on the metal on the aluminium surface. So, it will remain anode all the time. Now, this is 1 part and of course, in case of stainless steel apart from chromium, we add nickel, we add molybdenum, even we can add titanium, niobium. So, those all elements would provide bit of extra passivity or it can improve the passive layer improved in order to have a better resistance to corrosion.

When we talk about the improved the passive layer means it can modify the oxide layer. So, the diffusion of ions which is the metal ion to come from the metal layer or metal oxide film layer to the metal electrolyte to the oxide electrolyte interface. So, we have 3 interfaces, 1 interfaces this is rather two interface 1 is this is film oxide film this is metal this is electrolyte find in case of porous film on top of oxide film.

We can have 3 interfaces, there 1 interface will be oxide and porous film. So, what happens the metal ion so, this is the metal which is forming the oxide. So, this is the metal on top of oxide films of forming those metal ion migrates through the oxide film and comes to electrolyte and there it dissolves. So, if the oxide film is modified so that the diffusivity of this metal ion is reduced so of course it will reduce the corrosion rate of that metal.

Now, in addition in apart from that, we can have a few other aspects like to there are electrolytes which are very good passivator, for example, HNO3 then we can have HO3 Chloride then potassium chloride. So, potassium permanganate then potassium chromate. So, these are the even oxygen, they can passivate easily. Now, oxygen gas passivation is nothing but if it reacts with the metal and forms oxide layer.

And that would lead to a passivation. Now, say as some cell passivating elements for example, chromium, titanium, tantalum, and aluminium those are cell passivating element because they form oxide very quickly, because they have a very high affinity to oxygen and can form oxide layer. A few nanometre thin oxide layer and these oxides are very stable oxides and not very pervious oxide impervious.

I would say there are these oxides are impervious. So, the diffusivity of ions will be less and of course, it will other it will does reduce the corrosion rate of the metal. Now, how then third is once a metal is passive, it can maintain passive state if it is not disturbed. So, once metal becomes passive if it is not disturbed by some external force, it can maintain it’s passivity. So, I mean to say that for example, the classic example in case of Faraday's experiment.

Once we dip it in concentrated nitric acid and then we see that the passivation appears. And then we take that particular iron object into our dilute solution corrosion rate is negligible. So it maintains passivity and it will maintain passivity if we do not scratch it. If we scratch that particular metal object, the passivity is lost and it will not go back to the passive state if we do not put it back in the concentrated acid.

So then that case once we put a scratch in the dilute acid, it will go into the active state and it maintain its active state. So if we do not disturb it will maintain passivity. The other classic example is, let’s say 1 particular metal has passivated. Now in that solution if we had a little bit of halides, like chlorides, bromides those halides are even fluorides to halides are not a very good thing for passive layer to maintain it passivity.

And though halides layers halides to halide ions, they attack passive layer and disturbs the passive layer and break the passive layer. And that braking happens at localized portions. And once it happens at the localized portion that becomes a critical a very, very serious state, because that local region. So, for example, we have a passive layer, this is the passive layer. So, this is the layer, this is the metal surface, once we have a kind of break into the passive layer.

So, let’s say this is the break, so this zone is broken. So, that these zone we have exposed metal surface or this metal surface this metals portion is exposed to the electrolyte and that can happen due to the addition of halides, chloride, the bromides, those ions and now, around every all the segments. So, this particular segment are cover by oxide film and the inner the small segment is exposed to the electrolyte.

So, the small segment will be a small anode and as entire region is cathode, because entire region have oxide, so, oxides can be cathodic to the metal. So, now we have a tricky situation low anodic area since, this becomes a low anodic area and around this zone you have large cathode. So, that case the dissolution rate in this portion will be extremely high. So, we can have a very rapid pit formation.

And that pit growth could be auto catalytic in nature and that can lead to failure or catastrophic failure into the material. So, 1 classic example is in case of stainless steel, where the breakdown of the film can happen locally. And once that breakdown happens at local positions, that local region will act as anode, and it is a small anode and large cathode around that area.

So, there will be huge number of large number of cathodic reaction on the cathodic surfaces and to maintain the electron supplied to those cathode reactions. This anodic small anodic portion need to supply electrons to those cathodic area. So it has to dissolve rapidly. There are few factors which can lead to passivation. One is temperature, few factors just to name few. Temperature is an important aspect of passivation.

Many cases at room temperature one metal may not be passive, but in certain electrolyte, but if we reduce the temperature, it can go into passive region. For example, copper, it is not passive and concentrated HNO3, but if we reduce the temperature at room temperature of course, and if we reduce the temperature to around - 11 degrees Celsius in the same acid, it is passivate.

So, this is one example and then oxidizing or reducing environment. So, of course, if it is oxidizing that environment has good oxidizing power, many cases it can increase the corrosion rate for example, if we add oxidant like FeCl3 in HCL, the corrosion rate of zinc increases many fold but many a times addition of oxidizer like let's say HNO3 is a strong oxidiser.

So, that can lead to passivity okay. So, for example, in case of iron strong HNO3 oxidizing agent can lead to passivity and of course, reducing environment, it tries to break the passivity. Then third is cathodic polarization. So, we will talk about this cathodic polarization depending on sometimes, if some oxidation cathodic reaction is taking place, that reaction if we modify a bit.

It can either take me to active region or it can either take me to passive region depending on how that cathodic polarization graph or the plot is intersecting with the anodic portion of that particular metal, And of course third is abration or scratch. So, these are the mechanical effect, which can lead to break down a possibility. And finally, of course, if I consider there are many other factors.

I am just pointing some important aspects, finally ennoblement. So, ennoblement due to passivity, ennoblement happens that means, it can change its polarity. This is one instance other case the metal potential can, if we have very active state for example iron if it is active, the potential could be in the range of around - 600, 500 to 600 milli volt. That means I am talking about the corrosion potential.

And even if we try to see the OCP that means open circuit potential it remains around 600 milli volts region when it is active, but once it becomes passive, that time potential can reach to around 400 to 300 milli volt - of course, it is also in the - range, but the potential has moved to a positive side. So, that is what it is called ennoblement. But this ennoblement can lead to problems.

Sometimes for example, in case of zinc coating on iron. That is a typical example of why zinc coating should not be used at a higher temperature. If the temperature reaches around 60 to 70 degrees Celsius, at room temperature, at the normal temperature and 50 degrees Celsius till 60 degrees Celsius at least. Zinc acts as anode to iron so, that what it is a very good galvanizing material for protection of ion from corrosion.

But, once the temperature reaches beyond certain around 60 more than 60 to 70 degrees Celsius, zinc oxidizes and then it forms zinc oxide. Now, once zinc oxide forms, because we have this is my iron layer and this is zinc layer. So, once zinc forms zinc, remains a zinc if there is a break small break. Let’s say there is a small break. So, that break region that broken region the iron is exposed.

Iron is this is exposed iron is exposed to the electrolyte. This is electrolyte the corrosion can happen but we have already seen from the mixed potential theory that here iron preferentially acts as a cathode and zinc becomes anode. So, zinc dissolves and this section, is protected, fine. But at a higher temperature 70 degrees Celsius the zinc once it forms oxide, so that said this layer is forming zinc oxide.

So, then zinc oxide becomes cathodic to this small segment. So, the polarity reverses initially zinc was anode that, it was negative terminal in case of galvanic coupling, but, once it forms zinc oxide it becomes positive. So, it becomes cathodic to the positive terminal to the small opening into that layer or the coating. So, that case these segments will dissolve rapidly this segment will dissolve rapidly and zinc oxide will remain as cathodic layer.

So, these are the some of the criteria or the statements which are very true for when we discuss passivity, so we will keep discussing more about passivity. So let me stop here. Will continue our discussion on passivity in subsequent lectures. Thank you very much.