Corrosion – Part II
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Lecture – 26
Passivity

Let’s start lecture 26.

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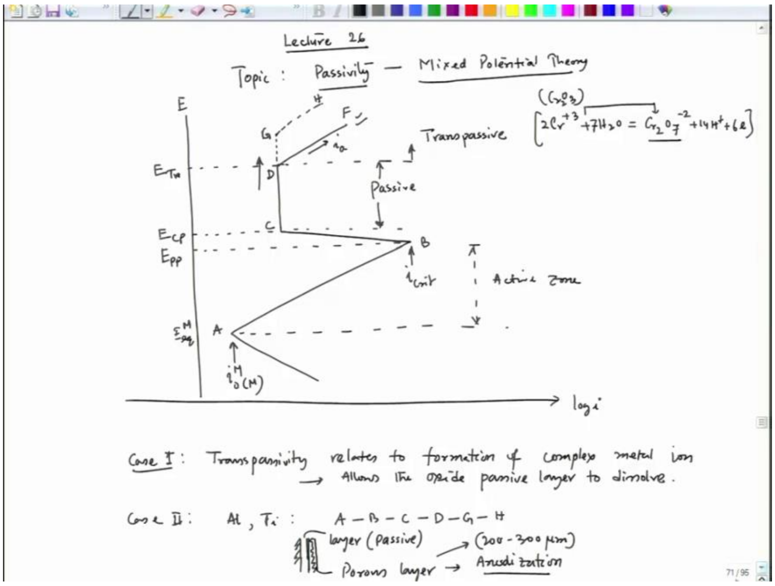

Lecture 26

Topic : Passivity — Mixed Potential Theory

Transpassive $[2Cr^{+3} + 7H_2O = Cr_2O_7^{-2} + 14H^+ + 6e]$ $((Cr_2O_3))$

Case I : Transpassivity relates to formation of complex metal ion → Allows the oxide passive layer to dissolve.

Case II : Al , Ti : A – B – C – D – G – H

layer (Passive) → (200 - 300 μm)

Porous layer → Anodization

And topic will continue our discussion on passivity and today will try to connect you to mix potential theory, fine. If we try to see the discussion what we had in our last lecture, this is the diagram what we have drawn. So, if we try to see only the, now we have seen that this zone is passive zone. Now, after that either we can have increase in current density due to Transpassivity or due to oxygen evolution reaction.

Or due to formation of porous film, or due to breakdown of passive film due to the effect of chloride ions are halide ions halides. So, now, if we try to pinpoint those points, those particular, let’s say if we start with transpassivity when you have transpassivity, the line starts moving towards right again and we have seen those zone. This is active zone, this is E equilibrium of metal and this is i zero M over M surface this is i critical.

And corresponding potential is Epp. We have Ecp which is complete polarization. Then we have E trans, okay. So, this is transpassive region. So, this particular region we call it transpassive and this particular thing can also appear due to if even if the transpassive that this metal oxide does not get affected or the it does not get broke down, there could be anodic plot like this increase in current density that could appear due to oxygen evolution.

But we are not talking about oxide evolution anymore assuming that this polarization line is not making across, connect cross it is not crossing the oxygen evolution line. So, if it happens like this, we have talked that metal forms or some complex metal ions, which will not have any protection ability rather it would try to dissolve. For example, one such example is chromium.

Now, chromium trivalent ion which is nothing but Cr2O3 which gives a protection in case of chromium. But, if it goes to a high potential, so, in case of chromium, a chromium passivation appears because of chromium oxide formation. Now, that trivalent chromium ion can react with H2O and then form Cr2O7 - 2 + 14 H+ + 6e. This reaction can happen, where this is the transition it can have where this one can dissolve.

So, the oxide layer will no more be passive rather it will start dissolving. So, this we are talking about with this we are indicating as a transpassive zone. Now, this is one instance. So, this is case 1 where transpassive relates to formation of complex metal ion which allows the oxide passive layer to dissolve, fine. So, this is case 1 and then you can have increase in dissolution again ia would further increase.

And then there could be another situation which appears case 2, this is case 1 and this is case 2. Let is say in case of aluminium if we increase the potential further then we can have if we increase the potential further the plot can be like let me pinpoint those points this is A, B, C, D, E. I am not using E because E is express as potential So, I can mention as F then this is G, H if I go in case of aluminium or titanium if I go for the positive potential.

If we take forcefully that metal to a positive polarized side polarization. If we allow that positive polarization anodic polarization to take place, so, the polarization line can go A, B, C, D, G and H at a higher polar potential. Since I am increasing the potential my layer thickness, this is the metal surface let’s say and this is the layer that is forming passive layer this is passive this layer is forming.

Now, as we are increasing the potential in order to maintain the constant electric field the thickness has to increase and when it increases there could be possibility of formation of a porous layer on top of this had adhered layer, so this is a porous layer that can form, okay. So, this porous layer when it forms we call it anodization, okay. So, this anodization or we call it anodizing or anodization.

So this anodization is related to some of the metals like titanium and aluminium. Since it is a porous layer, the dissolution rate further increases and this thickness of the porous layer could reach up to 200 to 300 micrometres, since it has to increase the thickness has to increase. So, that is what this porous layer forms this is anodization, okay. Now, again, if I consider case three.

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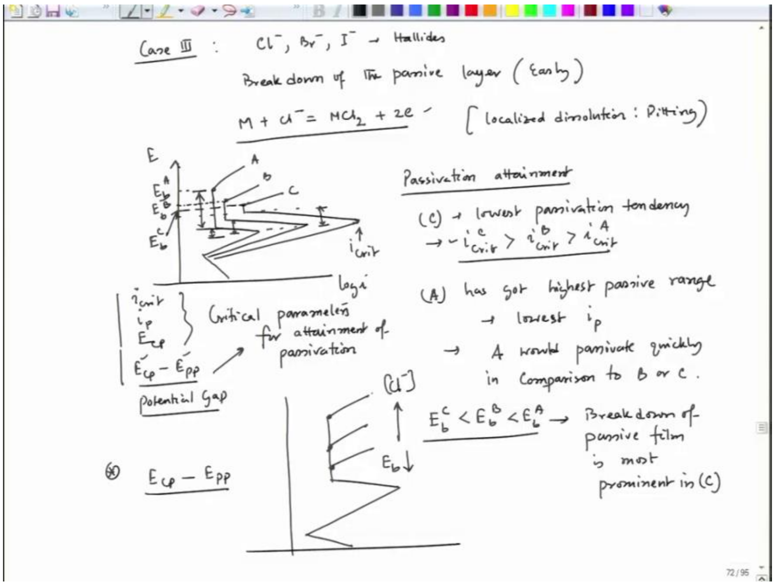

Case III : Cl^-, Br^-, I^- → Hallides

Break down of The passive layer (Early)

$M + Cl^- = MCl_2 + 2e^-$ [localized dissolution : Pitting)

Passivation attainment

(C) → lowest passivation tendency

→ ~ $i^C_{crit} > i^B_{crit} > i^A_{crit}$

(A) has got highest passive range

→ lowest i_p

→ A would passivate quickly in Comparison to B or C.

i_{crit}, i_p, E_{cp} } Critical parameters for attainment of passivation

$E_{cp} - E_{pp}$ Potential Gap

$E^C_b < E^B_b < E^A_b$ → Breakdown of passive film is most prominent in (C)

⊗ $E_{cp} - E_{pp}$

There could be a possibility of case 3, if the solution has chlorine, bromine or chloride bromide or iodide these are the halides if we have halides in the solution, then there could be breakdown of the passive layer and it happens early very early in the process. So like here, we can have a breakdown like this at this point. So this is we can write is that Eb E breakdown generally it is return the small form Eb and this is breakdown.

So this breakdown happens because of this reaction this metal it can react with chloride, which form metal chloride + 2e, so again we could see that it is a basically anodic process. And that is what the reaction again goes towards anodic side. And because of this, the anodic this metal oxide layer dissolves and this dissolution happens mostly localized dissolution which led to pitting, fine. So, this is another process that can happen, okay.

So, if the this particular segment this particular segment, I can have a very For example, let’s if I this is E, this is log i, the plot could be like this. I can have this and I am talking about breakdown part then it can have like this or it can have like this. Now, I could see that if I compare this three cases this is A, B, C. I can say that passivation attainment if I try to compare C has got lowest passivation tendency.

Why? Because it’s i critical because i critical of C is greater than i critical of B greater than i critical of A now, what it is makes, how does it make sense because, higher the i critical lower would be the formation of metal oxide layer on the surface and that would also reduce the tendency for the coverage of the metal oxide metal coverage of the metal surface. So, will not come across that situation.

Where the retardation of metal dissolution would be equal to the acceleration of metal dissolution and the retardation of metal dissolution as we have discussed it happens because of the coverage of metal surface by metal oxide. So, we need to have we need to go a very high current density and by that time it starts forming metal oxide because of the very rapid dissolution because i critical is nothing but the ia.

So, that means a very rapid dissolution takes place and there could be a surface perforation even below the rapid dissolution. So, we lose out the passivation. Now, coming to the other segment, if we try to see this breadth passive region breadth, they are also A has got higher passive range as well as it has or I would say highest among all three A, B, C lowest i passive that means passivity passive current density, okay.

So, it also indicates that it has A would passivate quickly in comparison to if we compare comparison to B or C and of course, B has a little better than C. So, that means, we could see that higher i critical is not good at the same time a wider passive region is good, but we have to also see that wider passive region should accompany a lower i passive. So, then we can say that metal has got a very good passivation tendency.

Now, if we try to see the breakdown, we could see the if this is the Eb so, this is Eb for A this is Eb for B and this is so, this is Eb for C and we could see that Eb C is lower than Eb B is lower than Eb A. So, this also indicates that breakdown of passive film is most prominent in C. So, the critical aspects if we consider we have to look at Ep, Ecp, ip and i critical.

So, these three are very critical parameters for attainment of passivation. Now, interestingly, we have been talking about these three quantities.

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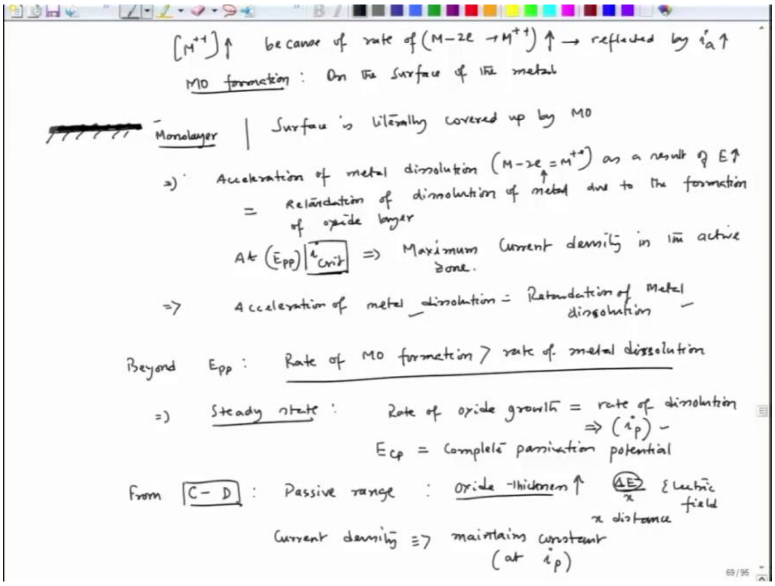

$[M^{++}]\uparrow$ because of rate of $(M - 2e \rightarrow M^{++})\uparrow \rightarrow$ reflected by $i_a\uparrow$

MO formation : On the surface of the metal

Monolayer | Surface is literally covered up by MO

$\Rightarrow$ Acceleration of metal dissolution $(M - 2e = M^{++})$ as a result of $E\uparrow$

= Retardation of dissolution of metal due to the formation of oxide layer

At (E_{pp}) $\boxed{i_{crit}}$ $\Rightarrow$ Maximum current density in the active zone.

$\Rightarrow$ Acceleration of metal dissolution = Retardation of metal dissolution –

Beyond E_{pp} : Rate of MO formation > rate of metal dissolution

$\Rightarrow$ Steady state : Rate of oxide growth = rate of dissolution $\Rightarrow (i_p)$ –

E_{cp} = Complete passivation potential

From $\boxed{C - D}$: Passive range : oxide thickness $\uparrow$ $\frac{\Delta E}{x}$ { Electric field

x distance

Current density $\Rightarrow$ maintains constant (at i_p)

But we have not yet discussed.

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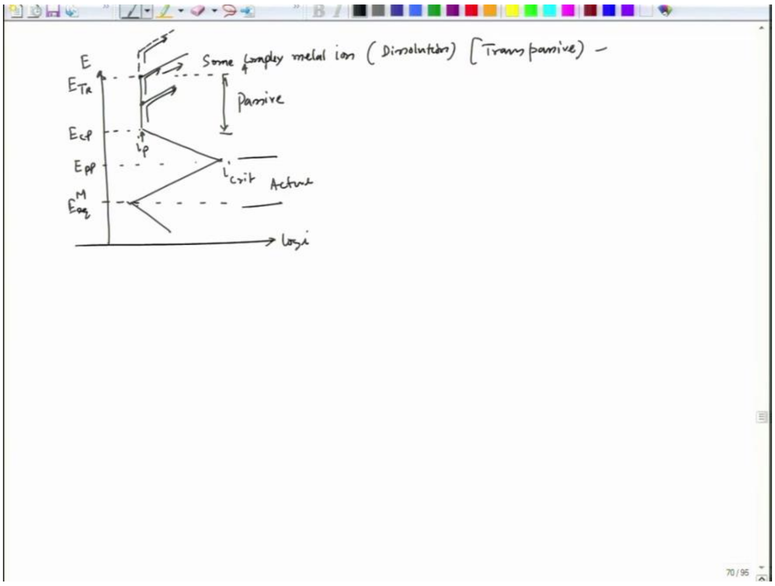

One important part which is this segment.

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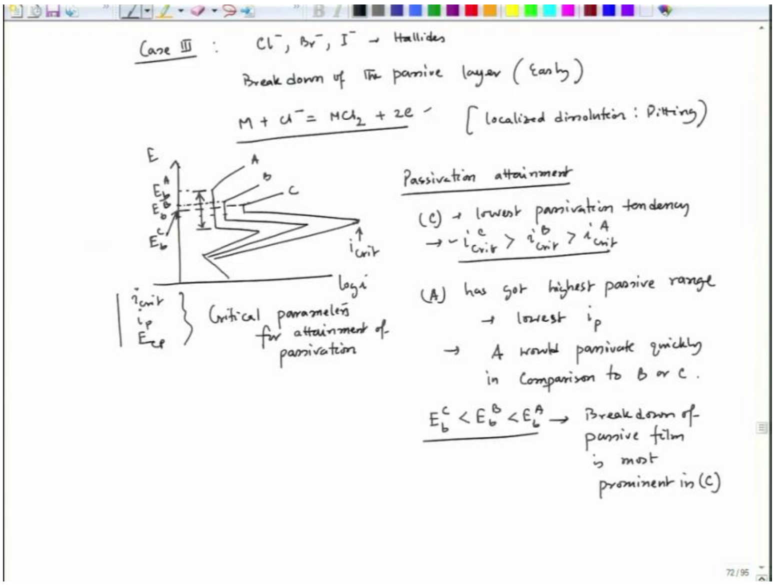

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$E_b^C < E_b^B < E_b^A$ → Breakdown of passive film is most prominent in (C)

So, which is basically the zone between Epp and Ecp So, we have to talk about Ecp and Epp these zone. This is a range of potential where, I could experience a growth of metal oxide and complete coverage of the metal surface. And then finally, will achieve to that situation where rate of oxide growth is just exactly equal to the rate of dissolution. Now, here if I tried to see. In order to understand the importance of this particular point and the relative position.

We have to introduce mix potential theory. Now, even without having a knowledge of mixed potential theory and the introduction of passivity and mixed potential theory, so, we can we could see that, in this case in case of A, this gap is minimum here the gap as we are going from A to B I could see that the gap is increasing. And in case of C it is the maximum this gap is increasing.

Now, what it does mean that in order to get to the passive region. That means in order to attain that ip I have to go to a much higher polarization before we could achieve that passivity. Now, why this breakdown is happening at an earlier state for example, if we try to compare us a kind of situation like this is one this is second this is third in the same metal.

I could experience this kind of situation we chlorine ion concentration increases Eb decreases. So, that means the breakdown potential reduces. So, there could be influence of increasing chlorine ion because and that could lead to decrease in breakdown potential or there could be inherent tendency of that metal oxide over that metal which could have a lower affinity to chloride or higher affinity to chloride if it is a having higher affinity to chloride.

Then it would immediately react with chloride ion and then dissolve into the solution. And that would lead to the breakdown of the passive film and lead to pitting. So, now, this gap is also another important factor. So, which is Ecp - Epp, so, this potential gap this is also critical parameter. Now, when we talk about the influence of when we will combine this passivation along with a way when you combine passivation with the mixed potential theory.

We would realize the importance of this Ecp and the Epp this gap. So, in order to do that.

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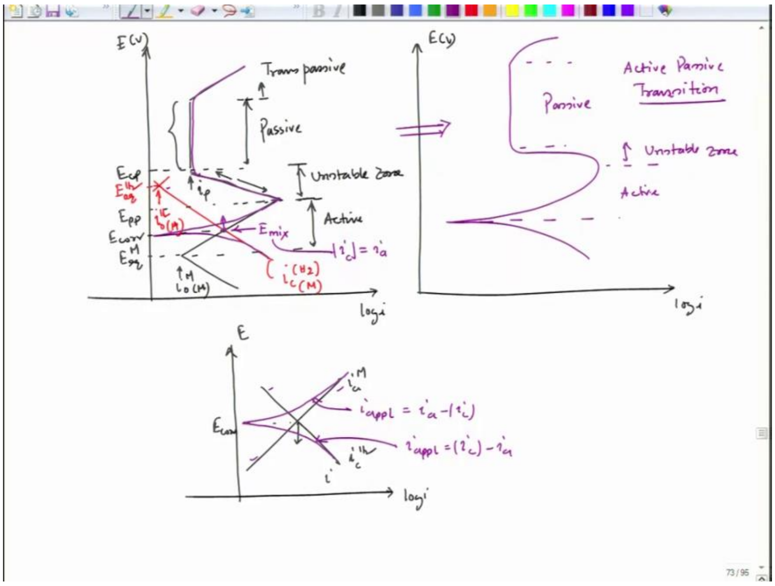

Let’s get to a simplistic situation like if we consider two situations this is E volt this is log i, this is log i this is E volt. Now, if the anodic polarization plot looks like this and let’s say we are not talking about oxygen evolution rather we are talking about transpassive region. So, this is transpassive and this is passive and this is active and these zone I can term it as unstable zone. Why this is unstable zone? This gap between Epp and Ecp.

This in this gap, the system has not attended the steady state yet, because we have talked about steady state in this zone and the metal has not achieved that steady state. So, in this zone is basically unstable zone if there is any disturbance in between the system can go back to this or if we continue if we there is no disturbance the system go towards this. So, I will talk about this disturbance what do we mean by this disturbance.

But at least one thing is appreciated here that we are trying to reach the steady state which is corresponding to ip. Now, if hydrogen evolution reaction interacts with this particular let me put this hydrogen evolution reaction in the form of red colour. So, this is the hydrogen evolution reaction which is ic hydrogen on metal surface. So, this is i zero of metal on metal and this is i zero hydrogen on metal surface.

This corresponds to E equilibrium hydrogen and this is corresponding to E equilibrium of metal when we have this now, as we have understood last time, when we talked about how do we get the experimental plot that said this is log i and this potential we have this two lines are intersecting this is ic hydrogen, this is ia of metal. So, we always divide in this case, this is E corr and in this case E corr is this one.

And here it is E corr and if we take polarization below E corr, so our plot nature would be like this, where this indicates i applied = ia - ic and this indicates i applied = ic - ia, because in this case ic is more than ia and in this case ia is more than ic. The same difference kind of this we have to take difference between these two currents, if we take difference, our graph pattern would look like this.

In this case, so, this is the E corr value, the graph pattern would be like this. Now, as we go higher and higher polarization from this, so, it will be same like this. Now, once it reaches to this, so, from there the current density further goes down, so, it will follow this track. And then since this is in the log scale so, the influence of this current density over this will be absolutely minimum.

So, then it will go like this and then move like this. So, what will be the plot nature the plot nature would be, fine. So, we are getting a experimental plot like this, which is basically the interaction of cathodic process and anodic process and here the cathodic process we have taken hydrogen evolution. And here this is the metal anodic polarization of the metal in the entire passive zone we have considered.

So, this is passive this is active and this zone is unstable zone. So, how we get the experimental plot that is also clear and that happens because of the mixed potential theory. So, the mix potential theory as per the mix potential theory, this is the point which corresponds to E mix and this is the point where I will have ic = ia and we get this curve. S, when we have this kind of plot, since it is going from active to passive, we call it active-passive transition. So, will talk more on this in our subsequent lectures. Let’s stop here, thank you very much.