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

Lecture - 31
Effect of Galvanic Coupling Between an Active-Passive Metal and a Noble Metal

Hello everyone. Today's lecture number is 31. And we will continue our discussion on passivation and mixed potential theory. So, we have discussed the effect of surface damage on the passive layer. At the same time, we have also discussed the effect of velocity in case of active-passive metals. Now, today we will talk about effect of galvanic coupling on the active-passive metal. So, today's lecture number is lecture 31.

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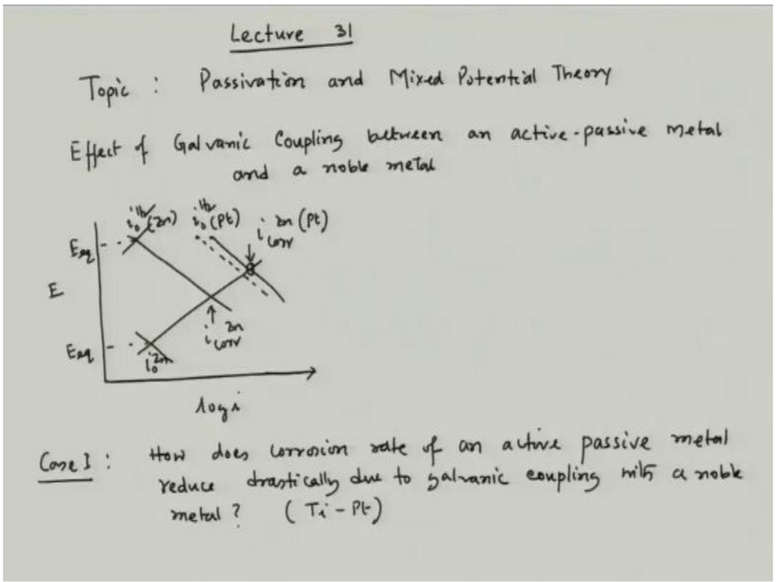

Lecture 31

Topic : Passivation and Mixed Potential Theory

Effect of Galvanic Coupling between an active-passive metal and a noble metal

Case I : How does corrosion rate of an active passive metal reduce drastically due to galvanic coupling with a noble metal ? (Ti - Pt)

And topic, passivation and mixed potential theory. And we will talk about effect of galvanic coupling between an active-passive metal and a noble metal. Now, in case of active metals, we have seen that, if we connect an active metal with a noble metal; like zinc connected to platinum or zinc connected to gold or zinc connected to palladium; we have always noticed that the corrosion rate increases.

And there you have to consider that equal area of both the metals are connected galvanically. And we have also understood that particular increase in corrosion rate of the active metal with the help of mixed potential theory. And if you recall, we have seen that, if we try to see the plot in case of, let’s say zinc is connected to platinum. So, this is E. This is log i. And if this becomes my active zone of zinc; so, this particular point is E equilibrium and i zero of zinc.

So, when if it is exposed to hydrogen ion containing electrolyte like acid, there it will have hydrogen evolution reaction on its surface. So, let’s say this is the hydrogen evolution reaction on its surface. So, this point become E equillibrium. And this is i zero hydrogen on zinc surface. And this becomes my i corr of zinc. Now, once we connect zinc, let’s say 1 centimeter square area with platinum of 1 centimeter square area.

Now, on platinum, the hydrogen exchange current density is much higher than that on zinc surface. But E equilibrium does not change, because this E equilibrium is decided by the pH of the solution. And provided the atmosphere, the hydrogen gas pressure is kept at 1. Now, if the exchange current density of hydrogen evolution on platinum surface is higher than hydrogen evolution reaction exchange current density on zinc surface; so, it will have its own polarization, cathodic polarization.

But you have to add all the cathodic current densities. And you have to see a mixed potential point where your total rate of cathodic reaction is equal to total rate of anodic reaction. So, that is what, we always add that particular hydrogen evolution reaction on zinc surface. And that particular goes like this. It is a parallel line, because it is in the log scale. So, now this point becomes my i corr zinc.

When it is galvanically connected to platinum of equal area, so that’s what the corrosion rate increases. But in case of active-passive metal, the situation could be different. There could be a situation that the corrosion rate either increases because of the galvanic coupling; or there could be situation that corrosion rate of the active-passive metal can decrease largely because of the galvanic coupling with a noble metal.

So, let’s consider the first incident where the corrosion rate of the active-passive metal reduces drastically, because of the interaction of the cathodic polarization of the cathodic reaction on that noble surface with the active-passive polarization curve of the, an active metal or of that particular anodic polarization side. So, if we; case 1, let’s see how does corrosion rate of an active-passive metal reduces, sorry reduce drastically due to galvanic coupling with a noble metal.

So, this particular incident happens in case of titanium-platinum alloy. Now, in case of this titanium is an active-passive metal. So, that means, its anodic portion first goes to an active region. Reaches i passive, this i critical, which is the maximum current density in its anodic polarization side. And then it reduces and reaches to i passive. And then continues; and finally, it has its own transpassive zone. Now, this typical plot for titanium metal;

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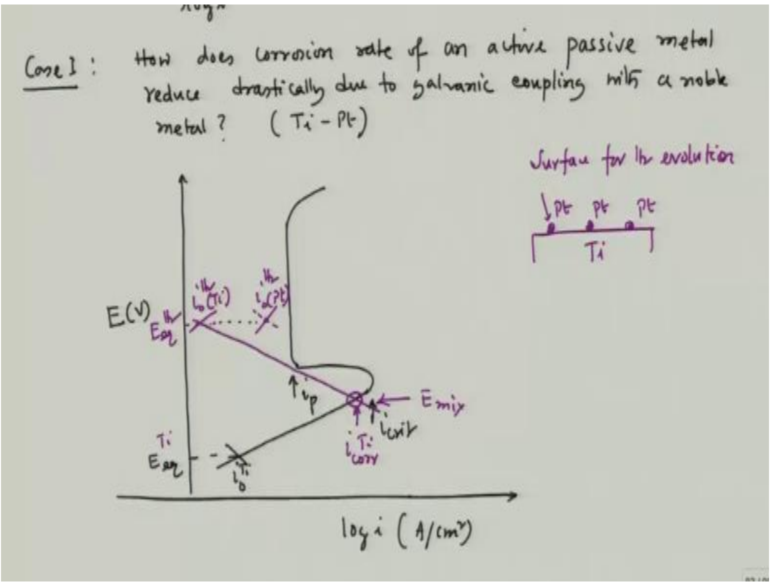

Case I : How does corrosion rate of an active passive metal reduce drastically due to galvanic coupling with a noble metal ? (Ti - Pt)

Surface for H₂ evolution

If I try to plot its E versus; this is volt; log i; let’s say this is ampere per centimeter square. I am just putting some unit. Now, the plot for titanium is typically like this. Fine. So, that means, we have i passive. Sorry, this is i critical. And this becomes my i passive. And these are the corresponding equilibrium voltage for titanium. This is i zero titanium on titanium surface. Or let’s say this titanium is showing passivity in an acid medium.

And the hydrogen evolution reaction becomes my cathodic reaction. So, on the titanium surface, we have, if I plot it with a different color; so, on the titanium surface, it can have its own. So, this is basically E equilibrium hydrogen and i zero hydrogen over titanium surface. So, this is the typical plot. And the interaction point is at this point. So, this becomes i corr titanium.

So, that means, if we leave it, if we leave one titanium piece in an electrolyte containing hydrogen ion, let’s say acid. And there, hydrogen evolution reaction, if it is the cathodic reaction. Due to the mutual polarization of titanium and hydrogen, both of them will try to drag the potential towards their, towards the mixed potential, which is the, mixed potential is, this one is the mixed potential, E mix.

And titanium has got a lower reduction potential, lower E equilibrium titanium than E hydrogen E equilibrium. So, that is what the corrosion rate is falling in the active zone of the polarization, anodic polarization side of titanium. Now, if we have platinum on titanium surface, then the platinum will provide surface for hydrogen evolution reaction. And again, this exchange current density of hydrogen evolution on platinum surface will come into picture.

Now, the hydrogen evolution reaction and it is exchange current density on titanium surface is lower than the exchange current density of hydrogen evolution reaction on platinum surface. And, but the potential or the equilibrium potential will not vary, because this is decided by pH of the solution, considering the fact that hydrogen gas atmosphere is at atmospheric pressure, which is 1 atmosphere.

Now, if the point which is the hydrogen evolution reaction point, which is the E equilibrium; so, this is the point and this is i zero hydrogen on platinum surface, provided the platinum is there on top of titanium surface. Okay. That means, if we have a titanium piece, if we have kind of dots of platinum on top of it. This is the titanium piece. Fine. So, these are the zones where platinum is locally present.

So, these provides surface for hydrogen evolution. And exchange current density of hydrogen evolution on these surfaces, platinum surfaces will be much higher than the hydrogen exchange current density on titanium surface. So now, on platinum surface, it will have its own polarization plot, okay, cathodic polarization. So, if the polarization plot is going like this; let's say this is the point that we shift just to give an better explanation. So, if I shift it here.

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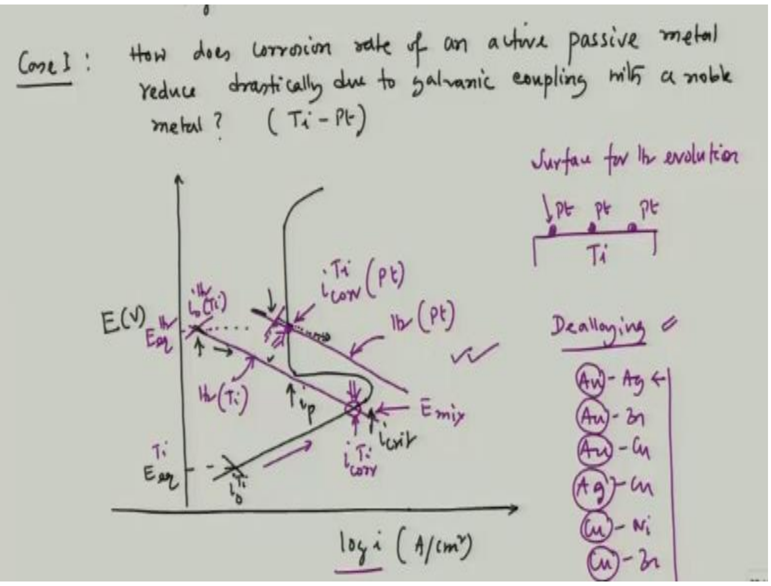

Case I : How does corrosion rate of an active passive metal reduce drastically due to galvanic coupling with a noble metal ? (Ti - Pt)

So now, this will move like this. Okay. So, this is the line. This is the hydrogen evolution on platinum surface. And this particular thing is hydrogen evolution on titanium surface. So, the mixed potential now falls on this particular section. Okay. So, at this particular, the anodic polarization curve for the titanium is being cut at in the passive region. So, the corrosion rate of titanium will be this, which is i corr titanium when it is galvanically connected to platinum. Okay.

And of course, when we have this platinum enriched zones on the surface, of course the initially, the titanium has to go through this line. This particular track will be followed. But in the beginning it will go to the maximum i critical region. And then finally it falls to this, because this is my mixed potential. Now, and then, I would definitely see that the corrosion rate when it was only titanium was at this location.

And after having platinum on top of titanium surface, corrosion rate becomes at this location; fine; in the passive zone. So, the corrosion rate decreases drastically because this is in the, it is in the log scale. Fine. So now, question is, how do we have platinum enrich regions or local spots on titanium. Now, for that, it is a kind of smart move I would say. So, we alloy, the titanium platinum alloy is formed.

And the platinum would be very less amount. Now, this particular alloy, if it is exposed to an electrolyte where titanium can dissolve preferentially, because the titanium is very active compared to platinum. So, titanium dissolves and leaving behind a platinum enrich zone on the surface. Now, this is a particular phenomenon called dealloying, which happens in case of gold-silver; in case of gold-zinc; in case of gold-copper; or in case of Ag-copper; even copper-nickel; we always have; or copper-zinc.

We always face a particular phenomenon called dealloying where active component goes to the solution in the form of ions. And the surface is enriched with a noble component. For example, in this case, surface will be enriched with gold. Here also, surface will be enriched with gold. All those cases, we see that, here in case Ag-copper system, Ag will be enriched; copper-zinc system, copper will be enriched.

Like that way, copper-nickel system, copper will be enriched. All those situations can happen. And this is the phenomenon called dealloying. This mechanism is not very simple. It is complicated. There are several such mechanisms. One of the mechanisms says that both the elements goes to the, go to the solution in the form of ions. Now, once both of them go to the solution in the form of ion, the ions which have higher reduction potential, they would like to go back to the surface of the metal and get reduced and form the pure metal.

And that is what those dot forms. And these, one dealloying metal is now-a-days used extensively in making porous material. Now, here also, the similar such situation happens. Initially, if we follow that mechanism, platinum and titanium both go to the solution in the form of ions. But platinum has got a much higher reduction potential than titanium ions. So, the platinum would get deposited on the surface in the form of a locally enriched platinum dots.

Those will then provide surface for enhanced hydrogen evolution rate. And that would lead to a situation like what we see in this particular diagram. And the corrosion rate reduces drastically, because the hydrogen evolution rate on the noble metal surface, in case of active metal, active-passive metal like titanium, it takes the mixed potential to the passive zone. So, this is one such phenomenon.

But there could be situation that even if it is active-passive metal, but still, because of the noble metal galvanic coupling, there could be increase in corrosion rate. And still there could be increase, even after having the, having this active-passive transition in that particular metal. So, let's see the second incident. In case of second incident, we can have an example of iron-platinum alloy.

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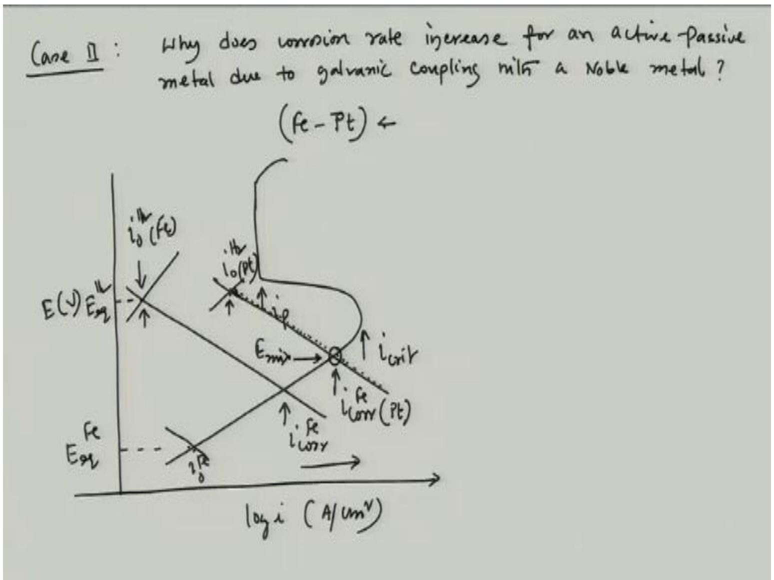

Case II : Why does corrosion rate increase for an active-passive metal due to galvanic coupling with a Noble metal ?

(Fe – Pt) ←

So, where the case, here the, we are talking about the case 2, where we are looking after a situation that, why does corrosion rate increase for an active-passive metal due to galvanic with a noble metal. So, in the previous case, we have seen why does corrosion rate of an active-passive metal reduce drastically, due to galvanic coupling with a noble metal. But here, the situation is, why does corrosion rate increase for an active-passive metal due to galvanic coupling with a noble metal.

So, that means, it is not a sacrosanct that if it is an active-passive metal, the corrosion rate would reduce. The main crux of the problem, main crux here is, where does mixed potential lies. That mixed potential, if it lies in the passive zone, due to the galvanic coupling with a noble metal; then the corrosion rate would reduce. But if the mixed potential lies in the active zone of an active-passive metal; because of the galvanic coupling with a noble metal; then the corrosion rate would increase.

Let's see a situation. This situation can arise in case of an alloy with a; let's say, in case of iron-platinum alloy. And here also, platinum enrichment can take place, if we do follow the dealloying concept. So now, let's say a platinum enrichment takes place. And then what happens? So, let's draw mixed potential, this Evans diagram, which is E volt, log i. This is ampere per centimeter square.

Iron is also an active-passive metal. And but here, the plot looks like this. Fine. So now here, this is my E equilibrium at iron. And this is i zero of iron in the acid solution. And this is of course passive zone. And this particular point is i critical. This is i passive. Now, if we consider hydrogen evolution reaction, since it is, this alloy is exposed to the acid. And hydrogen evolution reaction, let's say that becomes my cathodic reaction.

And let's say the E equilibrium lies here. And it will have its own cathodic polarization. So, let's say this becomes my i corr of iron when it is not galvanically coupled with the noble metal. Now, once this particular alloy is exposed to acid; so, this dealloying effect starts taking place. And redeposition of platinum takes place. So, there you have platinum enriched zones on top of iron surface.

So, once you have platinum enriched zones on the iron surface, those platinum will be acting as a center for increased hydrogen evolution. Because, exchange current density of hydrogen on platinum surface is much higher than that exchange current density of hydrogen evolution on iron surface. So, that increases; let’s say the increment is here. So, this becomes my, the new exchange current density of hydrogen on platinum surface.

And this becomes my hydrogen i zero, hydrogen on iron surface. Fine. Now interestingly, one thing I would like to mention. Here, if you see that, I have not added this particular current with this. Now, if you see that we have not added this particular current density with this current density. We have done it before. But this time we are not doing. That can be possible, if you see that this particular, the line between, this line and this particular line; these 2 lines are wide apart.

That means, the current density difference between these 2 lines would be very large. And if you take log scale in that particular current densities, the addition of the hydrogen evolution reaction on titanium surface would have very minimal effect on the hydrogen evolution reaction on platinum surface. So, that is what I have not added. But you can also add it. And that addition will be very close to it, very close to it.

Actually, it will be almost merging on top of the existing cathodic line on platinum surface. The same is true here. Here also, I, if these 2 particular points are lying wide apart, then we may not, even if we add these 2 current densities. Because the mixed potential theory says that the total rate of cathodic reaction should be equal to the total rate of anodic reaction at a mixed potential.

But here the, since these 2 current densities are wide apart and it is in the log scale, that particular addition would be very negligibly felt. So, I can have; since we consider that these 2 lines are wide apart; so, we can have a single line instead of double line. So, if this extend like this. Or you can also do the theory what we have done; but that particular point again would lie very close to it.

So, as if it is lying on top of the cathodic polarization of hydrogen on platinum surface. So now, this becomes my i corr of iron on platinum; when that iron piece is having galvanic coupling with platinum. So, now if you see in, even in spite of having an active-passive possibility of that iron; but because of the position of E equilibrium of hydrogen evolution reaction on; at the same time i zero of hydrogen evolution reaction on platinum and iron surface, the cathodic polarization line is cutting the iron activation line in the active zone.

So, that is what the corrosion rate is hiked or increasing. Okay. So, that means, there could be 2 possibilities. If the mixed potential lies on the passive zone, then I would reduce, I would be able to reduce the corrosion rate drastically. But if the i, E mix; this, because here, this is the E mix or mixed potential. So, this mixed potential, if it lies in active zone, of course the corrosion rate would increase rather than decrease.

So, these are the 2 situations we have experienced or we have explained also. So, let me stop here. We will continue our discussion on active-passive metal and mixed potential theory. But we will be finally discussing; we will be, in the next lecture, on the effect of, on the possibility of anodic protection in case of active-passive metal. And that particular anodic protection, we will be discussing with the help of mixed potential theory. So, let’s stop here. Thank you.