Aqueous Corrosion and its Control

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Lecture – 15
Forms of corrosion:
Galvanic or dissimilar metal corrosion (Part-II)

Welcome for the part II discussion on Galvanic corrosion. The part I discussion on galvanic corrosion we raised certain issues of like can we predict galvanic corrosion or not, if you have two metals? If you can predict can we determine a galvanic corrosion rates? And if these two questions are answered, then we said that you would like to know what are the factors that control the galvanic corrosion. And if you know what are the factors or parameters that control corrosion that effect corrosion.

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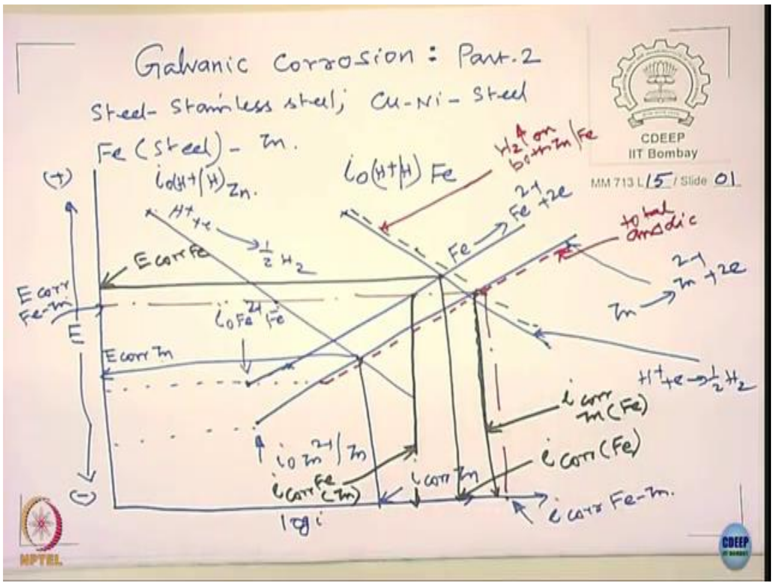

Galvanic Corrosion : Part.2
Steel- Stainless steel; Cu-Ni- Steel
Fe (Steel) - Zn.

Then it is easy for us to propose methods to avoid or to prevent the galvanic corrosion of the metals. We also need to look at the evaluation of the material for the application against the galvanic corrosion. We have seen the first aspect clearly in the earlier class, can we predict if two metals will undergo galvanic corrosion or not? What is the criteria for that? What is the criteria to show that I have given you let us say stainless steel and maybe a steel, between these two, one will be galvanically corroded. What is the criteria for that?

Student: It is a potential.

It is a potential. What is the potential called? It is a galvanic potentials are the corrosion potentials. So, we have seen in the last class that the galvanic potential is the primary reason for making one metal as an anode, the other one as a cathode. We also just started discussing on how do you really predict the rate of corrosion. We look at that in the Evans diagram all right.

We look at the Evans diagram taking an example of a clearly a noble metal and an active metal. We took for example, I think the platinum I think right we took platinum and then and then use the Evans diagram to find out what happens if I if you can coupled them galvanically with the other active metal. You know we gave only schematic thing there we did not give really actual values. I think we used what steel I suppose steel or iron is talked about.

Now, we also said that in the case of platinum the equilibrium that we deal with there is the I would say maybe H plus H H equilibria are maybe oxygen and hydroxide or water equilibria. For example, we are not really concerned about the platinum ion and platinum equilibria because too far from that.

And then we also looked at the equilibria what the equilibria of the active metal. In this case may be iron and iron ions and the corresponding tafel lines and see how the mixed potential theory will ultimately lead to the E_{corr} value of the platinum and the steel when they are coupled. What is the corresponding E_{corr} value? How as you get it? The same the mixed potential theory is valid here, the total amount of cathodic reaction on the system is equal to the total amount of what is that other reaction?

Student: (Refer Time: 04:44).

Anodic reaction. So, that is a criteria. If that is the criteria then you know what is the corresponding E_{corr} and i_{corr} values. We also said that if you are going to shorten platinum versus steel the E_{corr} value of the coupled, I mean the E_{corr} value of the iron goes up and so the anodic dissolution increases. We also say that the hydrogen evolution on steel or iron decreases; whereas, the hydrogen evolution platinum significantly increases.

So, these are observation that we made. In practice we do not normally see a noble metal being shorted with the active metals. We normally see metals which are generally active in nature we are not talking about it ok. Say some examples practically you will see you know you may have this steel you may have stainless steels or you may have cupronickel alloy you can have steel. I am you know we are talking about one of the prevalent place of galvanic corrosion is what is the

Student: (Refer Time: 06:06).

Heat exchangers. In heat exchangers you can have a steel shell, the stainless steel tube you may have cupronickel to tube and steel as a shell we can have. We can also have titanium and we can have steel titanium stainless steel this kind of combinations are quite common ok.

And so you are going to talk about really two active metals when they are involved, how does the corrosion takes place? Now**,** I am going to now talk about here between two metals which is let us say I will call I use iron here which is a somewhat like steel, I talk about a steel combined with the zinc.

In practice it is not the situation here you have a galvanized coating, but I do not think zinc is used as a structural material. You know there may be some zinc die castings, but otherwise structurally zinc is not used as a good material of construction. I taken zinc for what one important reason to show that i_{corr} is not important in the galvanic corrosion; you have two metals like a steel and zinc. If I have assume that the steel has got high corrosion rate and zinc has got low corrosion rate that is not going to decide the galvanic interaction.

What is going to decide is the galvanic potential that decides which is going to be made anode, which is more going to make it as a cathode. So, that is the reason why I chosen to illustrate how the galvanic interaction occurs between say iron or we can call as steel and the zinc.

Now, how do you proceed with? You proceed in this very simple similar manner like you draw two Evans diagrams right. The Evans diagram for what? Evans diagram for the steel the Evans diagram for zinc which is first you need to make them right. But when you making this be clear about what to you what to you in Evans diagram what are the things required, you need what are like exchange current density you require tafel lines are required terms of required, the equilibrium potentials are required these are the thing that are required actually.

So, what you can do is you can construct a Evans diagram for zinc and iron separately right or independently and find out between these two which will undergo more severe corrosion and when you short them when the galvanic interaction occurs right. What happens to these two metals? And so I think you can you can work independently now I think this is it you can start drawing the diagrams.

But keep in mind the one important factor, what is the difference between zinc and iron? We discuss I think which will undergo more corrosion zinc will undergo more corrosion or iron will more undergo more corrosion, let us say in an acid solution.

Student: (Refer Time: 09:42).

Yeah.

Student: (Refer Time: 09:43).

Which of the two or maybe in a let us say in a sodium chloride solution, where the hydrogen reduction reaction is the cathodic reaction and other is the metal oxidation. You tell me which of the two metals you expect to corrode more iron, why? Yeah, so the exchange current density for hydrogen.

Student: (Refer Time: 10:12).

Equilibrium so with H plus on zinc is much lower as compared to the exchange current density for H plus H on iron, it is about 10 power three times difference ok. So, then again now we can draw a typical or I would say a schematic reverse diagrams representing iron and steel and show how the corrosion taking place. I think you should draw parallelly and see how you are you are getting this things now.

So, I am just going in a very simple manner and there is nothing very complicated here right. So, I represent now the Tafel lines for hydrogen reduction reactions I will do that. So, which is what? Which one corresponds to iron and which one corresponds to zinc?

Student: (Refer Time: 11:56) Right.

The right one corresponds to?

Student: (Refer Time: 12:04).

The exchange current density for Fe 2 plus Fe and zinc and zinc 2 plus are almost the same 10 power minus 6 or so is not going to change much actually. So, I have just drawn a you know a kind of representative diagrams ok, which one will corresponds to zinc, which is the one correspond to iron?

Student: Lower one.

Lower one so this corresponds to zinc right $i^{o}_{Zn^{2+}/Zn}$and what is this is corresponds to i^{o} right. Now, you can find out what is the corresponding corrosion rates right and this is the i_{corr} zinc all right. What corresponds to iron? The iron comes somewhere here, see you please again label that you have to label these things otherwise it will be confusing, this corresponds to and this corresponds to the electrons right.

And these two are corresponding to what this is corresponding to and I have to put an arrow here this corresponds to right. How do I proceed further, how do I know when you do a galvanically shorting them? What will be the resultant corrosion rate of iron and zinc? How do you proceed? I have to add the oxidation of both the oxidation curves and I have to add the reduction curves corresponding to both the metal surfaces right.

So, I do that ok. So, what you can do is you can just add this two right and this corresponds to what? This corresponds to hydrogen evolution on both zinc and iron correct and similarly I can do this response to total anodic. So, what is happening now? It is this intersection point of this the mixed potential theory is now is valid right. So, I draw a line connecting all of them.

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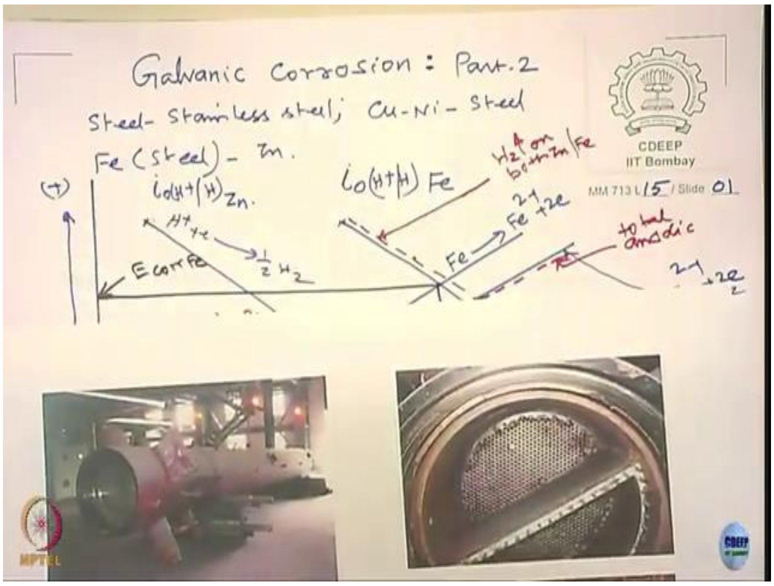

Galvanic Corrosion : Part.2

Steel- Stainless steel; Cu-Ni- Steel

Fe (Steel) - Zn.

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Then I draw this line what is this potential called? This is of E_{corr} of iron and zinc couple right. This is the i_{corr} of iron and zinc coupled, total corrosion rate is increasing actually right; I hope this lines are clear to you now. So, can you tell me that means what happens?

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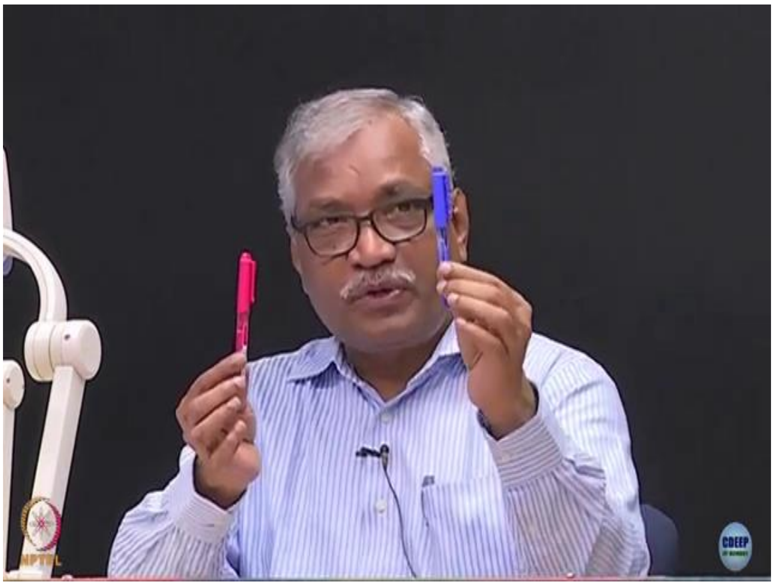

I take a zinc; I take zinc and I take iron here I determine this corrosion potential of that corrosion current of this. Now, I put them together I just short them like this, when I shorted will the potential of iron and zinc will be similar or different? It is similar because is conducting is conducting highly conducting. So, the potential of these two are going to be similar right, that potential of this corresponds to what is given in the Evans diagram as E_{corr} iron and zinc this what you will seeing this here.

At that particular potential what is the current that is flowing on steel and zinc is given by this diagram. Now, can you get from the diagram what is the one that corresponds to the dissolution of iron? What is the one that corresponds dissolution of iron and what is the one that corresponds to the dissolution of zinc? Can you people tell me in this what is happening there?

Student: (Refer Time: 20:08) Intersecting.

Yeah, so the line the potential line intersects now, where does it intersect? It intersects all the lines it intersects the cathodic reduction curve of iron zinc, anodic current of iron and as well as zinc

Student: Right.

Right. So, that particular intersection point gives you what is the corresponding reduction reaction, oxidation reaction in both cases ok. So, what is happening now? Now, what is happening now you see what is happening to hydrogen evolution on zinc on zinc, the hydrogen evolution on zinc is getting reduced to this value am I right.

It is reduced from here to this is value is getting reduced right. The hydrogen evolution is decreasing from here to here, but what is happening to corrosion? The corrosion of zinc is moving from here to this value, am I right. So, zinc is now getting oxidized more. So, this is your this is the i_{corr} of zinc and when coupled with iron right no I am sorry nothing wrong actually it is wrongly actually right ok. No yeah it is correct only yeah I am sorry it is correct; yeah it is correct.

So, it is that of the zinc here is correct right. So, this is the zinc dissolution rate given here and this is the dissolution rate of the this is the dissolution rate or i_{corr} of iron zinc actually right. So, the iron corrosion rate is decreasing from this point to this point am I right and the zinc corrosion rate is increasing from here to this. So, what we call this process, you discuss about one protection before the electrochemical protection of a metal right. What do you call this?

Student: (Refer Time: 22:48).

The sacrificial protection it is a cathodic protection on the metal by sacrificial action, zinc is getting dissolved at the expense of.

Student: Iron.

Iron right the iron is getting protected here ok. So, look at these diagrams it is a very busy slide I would say busy diagram actually, you have several information that you can draw from here. If in fact, you understand this you would understood the mixed potential theory in completion, I do not think you will have problem because it is the most complex Evans diagram that you can think of actually.

Now, you know that the dissolution of iron is getting reduced to from here to this, zinc is increased from here to this it has increasing here ok; no sorry zinc is it is moving from here to this actually ok. So, the so this is what happens. Now, you look at the kinetic factors that influence the corrosion of zinc. What influence of the corrosion of zinc? In this can you just tell me more each of them influence other one right iron influences zinc influences iron right.

You have iron has got two tafel kinetics one is the anodic kinetics corresponding to iron dissolution, please understand you have a cathodic kinetics corresponding to H plus giving rise to hydrogen iron has got two kinetics, for the zinc to dissolve which are the two kinetics influence very severely yeah.

Student: Hydrogen evolution iron.

Hydrogen evolution iron is severely affecting, that means the beta c the beta c of hydrogen evolution on iron is severely affecting this agreed. Then look at from the zinc point of view which kinetics of zinc is affecting the galvanic corrosion of zinc. Zinc has two kinetics tafel kinetics one is hydrogen evolution on zinc right, other is the zinc dissolution zinc to zinc 2 plus right; 2 Tafel slopes beta c for zinc dissolution and beta a for the I am sorry. Beta c for the hydrogen evolution on zinc and beta a which is the oxidation of zinc taking place.

Student: Beta a in this case.

Beta a is so the beta a of zinc is getting influenced more. So, please notice the beta c of the noble metal I can generalize it and I say noble I mean relatively noble. So, the beta c of the relatively noble metal with a c of the relatively noble metal and beta a of the relatively active metal. Decide the galvanic corrosion rate. Can you say that actually see beta c of the of the relatively noble metal, beta a of the relatively active metal decides the galvanic corrosion rate right.

Similarly, the i^o of the i^o for the cathodic reaction of the noble metal is more important than the i^o of the cathodic reaction of the relatively active metals. Similarly, you talk about i^o of the metal oxidation to metal reduction, you talk about it is more for the active metal than for the relatively noble metals.

So, this diagram this diagram that you see here this diagram you see here it talks about what are the governing factors for controlling the galvanic corrosion. Can we predict the corrosion rate? Can we do it if I give you this these all the Tafel parameters exchange current density. Is it possible for you to calculate by solving the equation? What will be the corrosion rate of iron before coupling with zinc and after coupling with zinc? Is it possible to do that by solving the equations or not possible to do that? I want to answer from you.

Student: (Refer Time: 27:48).

Possible; so it is possible. So, it is possible to calculate the corrosion rates based on the mixed potential theory, based on the Evans diagram ok what will be the corrosion rate of the galvanic couple in two different metals are existing at all. All we need are the independent governing equations, yeah.

Student: sir (Refer Time: 28:12) metals are coupled.

Yeah.

Student: (Refer Time: 28:13) that you are considered hydrogen evolution.

Yeah.

Student: So, the hydrogen is getting evolved irrespective of oxidization of iron or zinc.

That is right you can add one more complication. What happens suppose I have oxygen in the system? It’s a genuine question when metal is corroding in water you still have. So, you need to add one more complexities to that right add one more to this you can solve the equation right, you can write algorithm and solve it. It is not that difficult for you to do this. In fact, people do it is not that in academic exercise people do in the field, how the corrosion are taking place in the galvanic conditions right.

So, it is possible people do it because there are practical problems existing in the field ok. So, they use these governing equations to solve the galvanic interaction between the two different metals are done actually ok. To say then what kind of a life is possible all this you can do this with this equation? I hope you able to get this clarity in this Evans diagram, if not you please have a look at this go through more closely; if you have any problem you please do let me know ok.

If you understood this Evans diagram I think you have understood almost all the complex Evans diagrams that are possible in the corrosion processes of metals. Where there are galvanically taking place taking place by crevice process pitting process or all are following the Evans diagram the kinetics of that actually. If you are; if you are; if you are clear and we if you have any questions we can move forward ok. Anybody has any questions you please let me know. Yeah.

Student: How do we get the line corresponding to the total anodic reaction in the in the given graph? Total anodic sir.

Say total what do you do? See the current varies with respect to the potential right. So, what I do? Let us take the case here let us take this one this corresponds to what? This corresponds to iron dissolution, this is the equilibrium potential. When I move the potential to higher value, suppose I move the potential I move it to here. F or example, I move to this place this corresponds to this how do I get this? The Tafel line right eta is equal to plus beta log i by i^o right.

$$\eta = +\beta \log \frac{i}{i^o}$$

I can calculate I know equilibrium potential I know applied potentials I can calculate right. So, I get this line I get this line. Now, at this given potentials suppose let us take this particular potentials, I know this is the amount of current for iron dissolution this is the current for zinc dissolution.

There is a total current I am going to get. Suppose I take iron and take zinc together and pass current, apply same potential by using an ammeter that is the total current I will get it. So, I simply added these two and in a graphical way, but you can also do it by solving the equations by applying various potentials right. You know the equilibrium potential you can keep on at different potentials you can able to do that ok. So graphically you can do this, you can also do by having writing a proper algorithm and getting these values without any problems ok. So therefore I have done it ok.

See I have not added here please see here, below this is only one current and above this only the current goes up right. So, I have just done a simply a simple common I would say should understanding that how this will work at all actually yeah. See please here this is a log scale the log scale is you know marginal means it is a log value right.

Assume that it is 10 power minus 4 and this 10 power minus 3 you add it what happens? So, it will be you know 10 power minus 4 10 power minus 6 is going to be 1000 1001. For example so in graphically speaking it is a log scale it would have linear scale it would have just pushed equally right. So this is a log scale here, that is why you are getting this small variation otherwise is a significant variation that you are seeing that ok.

Of course compared to this is small variation no doubt because the log scale at all ok. So, please notice that this is a log scale that is why we have added here ok, only small. In fact, if you look at more closely you may not even go to this value it must be just touching the line only, because you know it is 10 power it is 10 power 3 times higher. So, is go into go into the third decimal point; so it is going to be less only actually ok.

So, basically you know it is a log scale this what it is yeah. Let us shall we move ok. So, this is how you understand and you can predict the calculate the corrosion rate of the of the metals. Let us make it a little bit more complex.

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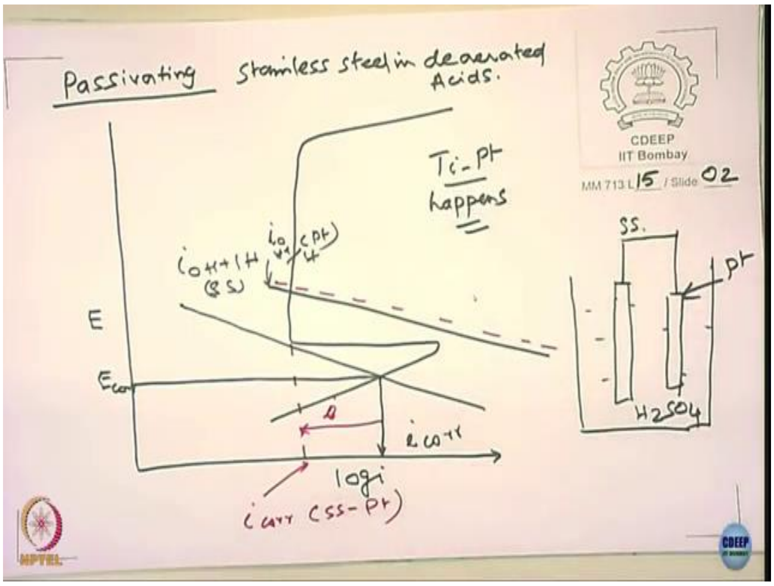

Assume that the system is passivating, you know the passive systems are. You know can you give an example of a passive system. Stainless steels in maybe in sulfuric acid ok, a titanium cannot be this ok. Let us take the case of a stainless steel in an acid solution, it is de aerated it is not aerated. So, what happens in that case? It undergoes. What it undergoes? Active passive transitions.

You have seen somewhere before, but is different way of interpreting today ok. Say, stainless steel in de aerated acids I am not talking about pitting at all just I will talk passivation ok. Let us take this what I want to do ok. So, this is corroding here the metal is undergoing, so this is let say $i^{o}_{H^+/H}$on stainless steels ok. This is in a active passive dissolution and you guys know that it is an i_{corr} this is your E_{corr}.

To make it pictorially I say taken a material in acid they say sulfuric acid dilute sulfuric acid. Now, the stainless steel, so this is the E_{corr} if I measure with the reference electrode and I get this E_{corr} and if you carry out polarization diagram all you get something like this actually. What I will do I am going to now insert a platinum and I am going to short this ok. What do you think will happen? Now, in order to know what to do happen what you should do now I should draw platinum.

So, I should do one for platinum what I have done for this I do one for platinum ok. I do something i^{o} on platinum. So, what you do? You just sum of these two. So, what do you think happens now corrosion decreases right, the corrosion rate significantly decreases because of the galvanic action right. So, you have to see that that the corrosion rate moves from there to this right. It is due to what it is due to i_{corr} of stainless steel platinum.

Understood for some reason assume that the lines going to lie somewhere here. Assume that line is going to somewhere here what happens what will happen increases. So, depends upon what extent the exchange current density is increasing, the exchange current density is not increasing adequately you could have a situation where the corrosion rate would increase right. Let us go to the situation here now it is moved from here to this does it reflect something we discussed earlier.

Student: Cathodic.

This cathodic protection is the potential is moving cathodic.

Student: (Refer Time: 38:25).

It is moving anodic right the potential is moving anodic. So, it is similar to a anodic protection. In anodic protection you are applying an external current by a potential start. Here you just use the platinum the platinum can able the passivation of metals possible, I am not saying doing but it is possible that you can do.

If this current is adequate enough to cross the nose of the diagram nose of this particular polarization curve, that that is of course is critical right. So, it is possible to do this and this is happening not here, this happens in the case of titanium and platinum; it happens in the case of titanium and platinum. We can take a titanium, the reason is that the E_p is quite low for that it is very low the critical current density for titanium to passivation becomes very small.

So, you do not need so much of so much of current required ok. So, the platinum it does help. So, titanium platinum is a well known example of industrial use industrially it is used actually. How is it used in industrially? I will just give a slightly different the people do is called as titanium platinum alloys its ok.

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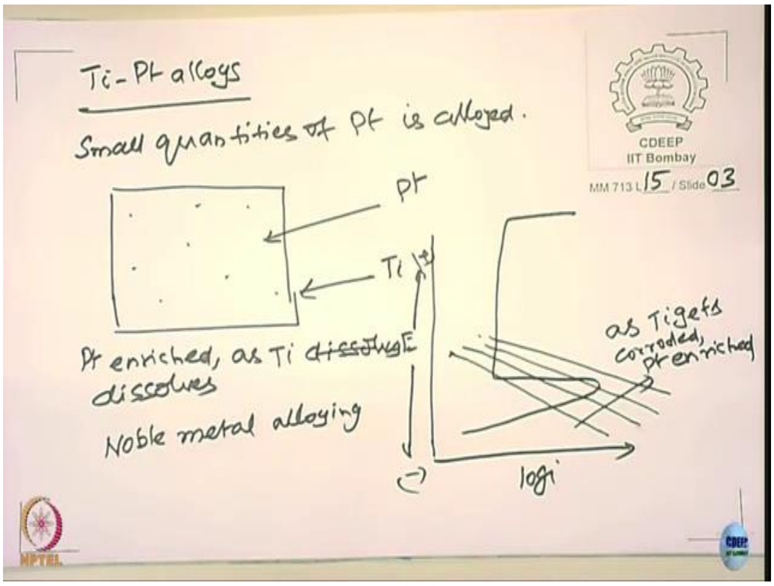

Ti-Pt alloys

Small quantities of Pt is alloyed.

Pt enriched, as Ti ~~dissolve~~ dissolves

Noble metal alloying

Here small quantities of small quantities platinum is alloyed, you make an alloy the metallurgists know right. You take titanium put platinum to that you melt it and this undergoes passivation. How does it go? I have let us say and I this is your titanium alloy and I have very small amount of platinum that I have.

How does it work? Initially in this case as I told you before I have this. Initially what happens? You get something like that. Now, as the titanium dissolves what happens? Platinum gets enriched right ok. Now, what happens as the titanium is getting enriched what will happened to this line? This line will start all right.

So, this will move as titanium it is corroded and platinum gets enriched. So, what will happen now in this case? At beyond certain point the platinum will beyond certain point the titanium will spontaneously passivate.

I do not need to pass any external current because of this. So, you do not put too much of platinum in the in the beginning you put small platinum ok, as a titanium dissolves enrichment of platinum occurs and so the cathodic curve starts shifting towards right side and ultimately lead to passivation.

Student: The hydrogen gets coated by mechanical of (Refer Time: 43:04).

Corrosion right, if it is mechanical action the titanium or platinum will go together right; it won’t remain platinum will also just get knocked off. Because platinum is noble it does not dissolve it remains on the surface and so it gets enriched ok. So, and this is called as; this is called this term for this is called as Noble metal alloying.

Student: Sir what is the electrolyte here?

It will mostly sulfuric acid.

Student: (Refer Time: 43:41).

Yeah reduction reaction is hydrogen only, in sulfuric acid right or a reduction reaction is a hydrogen reduction reaction actually right

Student: Reduction reaction that you are drawing these are the combined.

Yeah of course you can you can put a platinum and draw it, I just simplified all this section you put that. So, this you can say if you want is called as a noble metal alloying and so these the principles like this only.

So, what you need to look at here is analyze the situation ok, how does the galvanic interaction works? Ok. It could work if it is going to be purely noble metal and a active metal to different active metals or you can have a noble metal and a passive metal the passive metal and a active metal.

You know you can have all kind of combination you do not have to worry we just have to draw the Evans diagram and then find out what is the resultant galvanic corrosion can happen in the metal actually ok. So, that is the way you should proceed in calculating computing the corrosion rate of the galvanic couples ok; is it clear to you ok.

So, so far we have seen the influence of the electrochemical factors on the galvanic corrosion of two dissimilar metals. If I can summarize what are the factors that one should look into when you are computing the galvanic corrosion I think that will be very useful.

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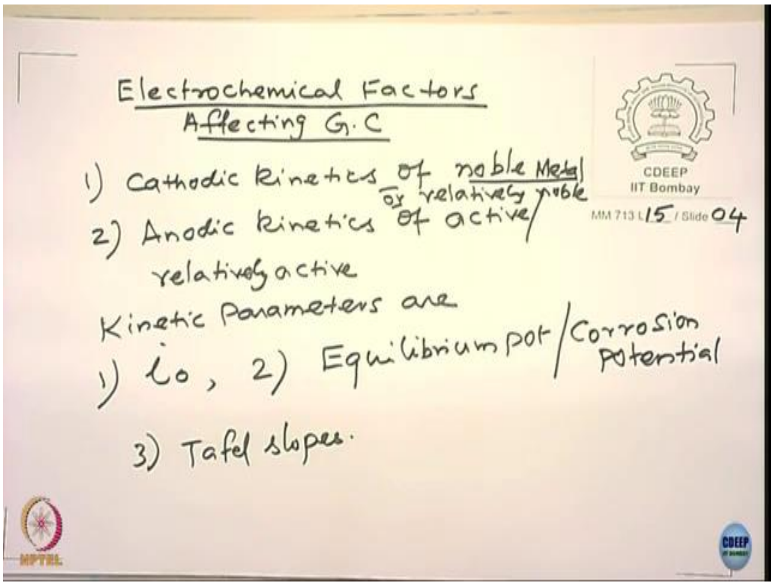

Electrochemical Factors
Affecting G.C

1) Cathodic kinetics of noble Metal or relatively noble
2) Anodic kinetics of active/ relatively active

Kinetic Parameters are
1) i_o, 2) Equilibrium pot / Corrosion potential
3) Tafel slopes.

The following factors electrochemical factors. We have seen three different cases, active metal and a noble metal to active metals in another case a passive system and the noble metal combinations. If I summarize what are the governing kinetics in each case? We can say that the cathodic kinetics of what metal you think which of the two the noble or active metal will influence the galvanic corrosion, the cathodic and it is a which one?

Student: Noble metal.

The noble metal of noble metal to the anodic kinetics of which of the two ok. I will put it as active or I called as relatively active that way you can even call this is noble or what you call it or relatively noble right; noble or it could be relatively noble. When you say this kinetics what do you mean by that what are the parameters you think they are broad right?

Kinetic means what are the parameters you think. What are the things that you will take into account? The kinetic parameters are what? One the exchange current density right; two what is that? It is the Equilibrium potentials or you may even called as a corrosion potentials. What else?

Third Tafel slopes right. So, you can look for these informations with respect to the relatively active metal and relatively noble metal and you get these parameters you can calculate what can be the galvanic corrosion rate of the relatively active metal right. So, that can be done without much of a difficulty. Any questions here? Ok.