Indian Institute of Technology Kanpur

Present

NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Module Lecture 011

Broad Subject: Solved problems on the corrosion rate, Exchange current density

Prof. Kallol Mondal

Dept. of Materials Science and Engineering

Let us continue with the problem what we have started solving in the previous lecture. The problem says that if the current density or the icor that is the current density for corrosion of iron is 1.69 into 10 to the power -4 ampere per centimeter. Now this is in case of iron. We know a few data one is atomic weight of iron is 55.85 and density of iron is 7.86 gram per centimeter cue. Now in case of mpy the unit says that it's milli-inch per year. So now we have to use the formula i into atomic weight of iron divided it is to be divided by nF in this case the corrosion is taking place in this mode. So n is 2 so let me replace n with 2. F is one Faraday and then we have to divide this term with density Rho of iron then we will get the unit length by time and now all those things let us put all those values of e, atomic weight, density of iron, and the current density and then converted into mpy unit.

Now 1.69 into 10 to the power -4 ampere centimeter square then this is 55.85 gram divided it is to be 2 into 96500 into 7.86 gram per centimeter cue. So this we have to convert into mpy which is nothing but milli-inch per year. So we have to convert all the things into milli-inch term as well as the time part. Here the time is hidden in this section because current is nothing but the rate of charge flow. So this we can write that 1.69 into 10 to the power -4 Coulomb per centimeter square per second into 55.85 gram, 2 into now this 96500 Coulomb is basically the gram equivalent which is nothing but the charge required to have a corrosion of one gram equivalent.

So 96500 Coulomb into 7.86 gram per centimeter cue. Now this two term canceled, now this centimeter now you will see that this one and this thing are getting canceled and gram and gram both are getting canceled. Now this is I'm putting it in bracket. Now second you convert into year. One second would be equal to 1 divided by 24 into 365 days in one day 24 hours into 60 seconds 60 minutes into 60 seconds. So this is the year. So one second would be this much year. So now if you put all the things and then later also you have to convert it into milli-inch so one centimeter is equal to 1/2.54 inch so if you would like to convert into milli-inch so 10 to the power of 3 milli-inch. So now you put all things in this then you would get let me put all the values and then you will see that the unit what is coming out after calculation is nothing but the milli-inch per year. So 1.69 into 10 to the power -4 into 55.85 into 10 to the power 3 into 24 into 365 into 60 into 60, it is to be divided by 2 into 96500 into 7.86 into 2.54 then you will see that this is coming out to be 77.251 milli-inch per year which is nothing but mpy.

So now if you know the current density the rate at which since we know the current density is nothing but the rate at which corrosion is happening, so then you can convert it into mpy unit and also mdd unit according to your choice. So now this is basically from the current density to mpy. Now let me put one more problem, let me solve one more problem that is the corrosion rate of an alloy. So this is for pure metal. It's very easy. You have to take the atomic weight of the pure metal and then accordingly you can calculate what is the corrosion rate.

Now in case of alloy you have to take we have already seen that in case of alloy you have to take equivalent gram equivalent for the alloy. How to calculate gram equivalent for the alloy? Let's say if it is AxByCz this is my alloy where A, B, C are three different elements and x,y,z they are in weight percentage and x+y+z equal to nothing but hundred in case of weight percentage and A, B, C's are elements.

If you would like to find out what would be my equivalent which is nothing but this formula you have to use, a/n, a is basically the in case of pure metal a is the atomic weight but since we are considering an alloy so you have to find out the equivalent which is – can be determined from this formula. If fi let me put since i you have considered for current density so let me put j in order to have a different notations are fj into Mj/nj. Now j is nothing but jth element. Let's say if you consider A to be the element then A would be first element, B would be the second element, C would be the third element so j value in this case would be three. So three elements for example one, two, three it will take three values, one, two, three. Now if you this is equivalent. This is gram equivalent for the alloy.

Now if j is nothing but the fraction of that particular jth element let's say if you consider A element the fraction would be x. If you consider B element fraction would be y and accordingly for C, fraction would be z. and nj is the let's say A is coming out by forming ions. Then you have to see what is the reaction there. The A can come out like An++ne so then that case nj is for A element is n. Now if n value comes out to be two then this would be two so in case of A element n would be two.

Now for this element like that so you can find out what is my equivalent. Now again let's say you would like to find out what is the expression of corrosion rate in the form of mpy that case you need to know what is my density. Now again you can also find out density by doing experiment but one way to find out density is again you can use another formula, density of alloy which you can take it as fj into Rho j. So here fj is the fraction of the element you are considering and Rho j is the density of that jth element.

Now like that you can find out Rho of that alloy. Since you have to use the formula here it is written so in that case this aFe it will be converted into a/n equivalent. Now here the in case of iron the equivalent is a by two, aFe/2 but in case of alloy it would be a/n. So you don't have to put the n value separately. Now let me find out one such chalk out one such problem. Let's say AISI 316 alloy this alloy. Now I know what are the fractions of different elements. Chromium is 18% and all are in weight percentage. This is weight percent. 18%, Nickel is 8%, molybdenum

3% and Fe 70%. So now you are seeing that let me calculate 18+8, 26+3 so if you can and 1% could be some impurity elements but that will not be very crucial for the overall calculation. Let me see that this is my overall composition. You can also put it as 71% no problem with that but let me ahead with this because now I can find out what is my n for different elements if it goes in the solution. So n let us assume that the n is in this case 1. n means the way the element is going into the solution in the form of ion. Let's say chromium then it go as +1+1e like that it would move. Nickel n is 2. molybdenum n is 1, iron n is 2. If I assume those values then I can also I know also the density of different elements. This is 7.1 gram per centimeter cue. This is 8.9 gram per centimeter cue. This is 10.2 gram per centimeter cue and this is 7.86 gram per centimeter cue. Also we know what are the atomic weight. Atomic mass of this elements. This is let us say A element so here it is 52.01 gram per mole. Now this is 58.68 gram. 95.95 and this is 55.85.

Now with this data set I can also find out what is my gram equivalent. Now a/n would be equal to then 0.1 --the formula we would be using that is fj.aj/nj aj is basically the atomic weight of that element jth element. So 0.18 for chromium. It's 0.18 into 52.01 by 1 plus 0.08 into 58.68 because this is percentage so you have to divide with hundred and then this is 2+0.03 into 95.95 divided by one plus 0.7 into 55.85 by two. Now this I can find out what is my value. This is 34.135 gram. Now for this if I know that the corrosion rate in the current density term if it is given as one micro ampere per centimeter square so this is my icorr. So in this alloy I know the icorr so I have to find out in the form of mpy. So that case I know this I can also find out what is my Rho. Let me note down this a value, a/n equivalent equal to 34.135 gram.

Now similar way I can find out what is my Rho of the alloy. So this is 0.18 into the Rho chromium 7.01 like that 0.08 into 8.9 plus 0.03 into 10.2 plus 0.7 into 7.86. So now from that you can find out my Rho of the alloy would be 7.7818. So let me put two up to three decimal let me take gram per centimeter cue. So I can also note down what is my Rho of that alloy is nothing but 7.782 gram per centimeter cue.

Now we know that in case of pure metal this is my formula to convert -- to have corrosion rate expression in the form of length by time. Now in this case I have taken aFe now if you take this ratio, this ratio is nothing but the gram equivalent. Now in this case in case of so the modified equation for the alloy would be i into a/n equivalent divided by F which is Faraday into Rho, in this case Rho of the alloy you have to take, Rho of alloy. So now you have to put now all the values and do the same treatment the way the treatment has been done for the conversion of units. You would get – this value is coming out to the 0.56 mpy. And you have to put this 1 micro ampere per centimeter square that means 10 to the power -6 ampere per centimeter square and you put this value, you put this value in this case and for Rho alloy this one the value, this is the value of 1 Faraday is 96500 Coulomb per gram equivalent.

So you would get this is my the corrosion rate expression in the form of mpy. If you would like to do in the form of mdd that case you don't have to use Rho alloy because if you divide this thing with the Rho then it would come the length the unit would come in terms of length penetrated, penetration depth per unit time but if you don't use this then it would be mass lost per unit time per unit area. So that you can also convert into mdd which is milligram per day per decimeter square. So this is about the rate expression for corrosion.

Now let us keep continuing with kinetics of corrosion. Now we know the concept of single electrode potential and not that too in the reversible condition and in the standard state E0, E0, M+n/M this is standard reduction potential and what does it mean, it means that if you have one unit if your concentration is one unit, unit activity or unit activity and temperature is 25 degree Celsius, pressure is one atmosphere pressure, that time if you measure the reduction potential then this value is coming; the value which will come out that would be termed as E0 which is standard reduction potential for that particular metal or particular element. Now what does it mean? It means that Mn++ne going to M. Now there is a equilibrium – there is an equilibrium between Mn+ ion and M.

Now if you see the metal surface this is my metal surface, now when the metal surface it forms metal ion so it leaves metal ion n+ so like that you can have Mn+, Mn+, Mn+ so you can have over the entire exposed surface you can have a section where you have Mn+ ion layer and on the other side its metal surface. Now you have two sections one is metal section one is ion section, positive ion section and there is an equilibrium that means the metal ion that is forming from the metal surface the rate at which it is forming or you can say the flux of metal atom that is coming out from the metal surface and forming metal ion n+ ion the rate at which that is forming that means the flux which is nothing but let us say mole per centimeter square per second; that means the flux which is the number of moles per unit area per unit second, so that flux the way it is forming this side and the similar way the metal ion also is getting reduced and forming metal. So flux at which this is going into this and this is going into n+ plus ion those two fluxes are same. So that suggests that the the system is at equilibrium and that too is happening at particular temperature and pressure.

Now when you have this let's say I am considering only this part. This part means a sort of deposition. Metal ion is depositing on the metal surface again. Now if you consider this section then metal is coming out and forming metal ion. Now we know what is the corrosion rate expression. The metal ion formation is nothing but the corrosion and also we know that corrosion is if you would like to find out what is my rate of corrosion or the rate of formation of metal ion formation that is nothing but the current density which is current density. Now once you know the current density you know that what is that my rate of reaction.

Again if you would like to find out the amount of metal ion that is forming per unit area per unit time then also you can have conversion which is nothing but i a off that metal which is atomic weight of that metal divided by nF, and in this case the number of electron that is participating in this reaction is n. Now this is my rate of reaction. At the same time when it is at equilibrium, so the rate at which this is forming and rate at which metal is forming so this is my rate, actual rate in terms of weight or mass loss per unit area per unit time if metal is forming metal ion and if metal ion is forming metal which is nothing but the reduction process that time the rate at which the metal ion is depositing both are same at equilibrium.

So I can write in terms of current density I can write that let us say if ia let me put it as a which is small a, i subscript a what a means nothing but anodic reaction. Anodic process means where oxidation occurs and oxidation means metal is forming in metal ion. So same way I can term this rate, this rate I can term it as ia which is nothing but the anodic process or the oxidation process. Similar way I can make I can give another terminology for the reduction process which is nothing but the cathodic reaction. So I can term it as if I would like to find out what is the rate of cathodic reaction I can term it as ic which is c is nothing but small c i subscript small c cathodic process. Cathodic process.

Now when if you would like to find out what is my rate of anodic process, ia a of metal which is atomic weight of metal, nF and I can find out this is anodic rate and cathodic rate is ic into a of

M divided by nF. So if these two rates are different so definitely these two terms would be different but at equilibrium I can have the same rate of this reaction forward as well as forward reaction as well as backward reaction. So that case I will have a relation between these two which is nothing but equal. This is at equilibrium.

Now if you consider the standard reduction potential that case you don't have any corrosion because you already meant – you have already maintained one unit activity to be one the metal ion concentration in the solution. So you have equilibrium between those many atoms, those many ions in the solution with the metal surface. So it is something like non corroding system because the rate at which metal ion is forming the rate at the same rate metal is also – metal ion is also getting deposited. So it's a kind of non corroding system and a reversible system. So that case I see that this value, this value both are same. This value, this value both are same. So this two are getting canceled at equilibrium so ia equal to ic.

Now if you have this I can term it as i0 provided the system is at non-corroding system and reversible condition. So that time I term it as i0 which is ia equal to ic equal to i0 and then this is i0 is considered to be exchange current density. This is considered to be exchange current density. Now we see this relation. Now there is one thing that is inherent into it but we have to make it clear what is the inherent part? If you see the direction of ia and ic these two directions are opposite in nature. For example ia is this direction, ic is this direction. So they are opposite. Though the values are same if you take mod value these two values are same but if you don't take mod then the magnitudes are same but you have a sign difference.

So the convention is it is the negative sign is considered in front it's written in front of ic in order to just indicate that ic is having opposite direction to the ia. So actual expression would be ia equal -ic. This minus sign indicates the direction of the flow of the charge or the current and either i0 is nothing but exchange current density when I ia equal to -ic in the reversible non-corroding process. So that time we term it as exchange current density, and this exchange current density has a huge implication on the corrosion process.

So exchange current density is one important one important kinetic parameter for corrosion process. Now in order to see the implication of exchange current density let me see one situation. Let's see you have same reaction n++ne, M now you can have a concentration cell where you have the same metal dipped in a solution of M+ ion, Mn+ ion this is the same metal. Now the same another cell you create where you dip the same metal into another solution where the metal Mn+ you are maintaining and now here the concentration is C1 and here the concentration is C2 and C1 not equal to C2. See if you connect it with a salt bridge and then connect with external wire then you will see the current is flowing. You have connected these two metal rods same metal rods. Those are dipped in two different solutions, same solution, solution with a different concentration of n+ ion and you have made the circuit complete. You will see the current is flowing, and this current will flow if C2 greater than C1 you will see that current is flowing from this end to this end. If you have more C2 more than C1 you will see that reduction potential at this electrode is more than reduction potential at this electrode. So current will flow from higher potential to a lower potential.

Now let's say these two areas which is exposed to the solution those are different. Now the external source, external circuit the current is I. Now here the exposed surface is you A1, here A2 and here the exposed surfaces A1. Now the same current is flowing through those two electrodes but the exposed area to the surface to the solution are different for those two metal surfaces. Now what would be my current - anodic current and cathodic current you can – if you are considering this it to be anodic current the opposite you can consider it as a cathodic current. So Ia equal to Ic but if you would like to find out what is my current density then Ia divided by the anodic area is this one, A1 and Ia, Ic divided by A2. Now I know the same current is flowing through those two electrodes but if you would like to find out what is my current density this is my current density on the anodic surface.

This is my current density on the cathodic surface. I can write it as ia small ia which is current density, this is small ic with a notation with this negative sign. Now do you think that this two are equal? Because these two are definitely unequal. Now if these are not equal so though the same current is flowing but you will see that the rate at which cathodic reaction is taking place is entirely different than the rate at which anodic process is taking place and that is happening because just because of different area, exposed area on the two metal surfaces. So here it is very important you will come to know later that if you couple copper and iron then you will see that let's say you have a copper plate, two copper plate you have riveted this to cooperate with the iron section iron rivet then you will experience the effect of this ia and ic on this particular structure.

So we were discussing about this iron rivet. You are using – if iron rivet is used to fasten two copper plates and that is in the seawater system. Now this situation would be very crucial. The current density would be very crucial not the current value. If you see here the current in the circuit it will be a closed circuit so current in the circuit would be same. The current what is flowing through iron iron rivet and the flowing through the copper rivet both are same but since now the amount of cathodic reaction if you consider that reaction is taking place over the entire copper plate and in this case copper this is copper plate, the copper plate is acting as the cathodic surface and the cathodic reaction will always happen on the cathodic surface. So here the cathodic reaction is taking place and of course if it is in seawater the cathodic reaction would be oxygen reduction.

So in this case cathodic reaction would be O_2+2H_2O+4e going to $4OH^-$ so this is a cathodic reaction in case of neutral solution since seawater is a neutral solution. So cathodic reaction is taking place over the entire cathodic area, and accordingly if these reaction is happening over the entire cathode surface and if you compare the area ratio of cathodic section and anodic section here the iron is acting as the anodic area and anodic reaction is definitely iron plus iron going to $Fe^{++}+2e$. This reaction is taking place on the anodic surface and if you compare the galvanic series I will come to that galvanic series later on. So this copper and iron if you couple them galvanically then you will see that copper is acting as a cathode and iron is acting as anode and once I really acting as anode so anodic reaction will take place on the iron surface. Now here two things. One is you have huge surface area for cathodic reaction. So now you have huge amount of electrons that would be needed for this cathodic reaction. So where from these electrons will come? These electrons will come from these anodic reactions.

So you have to have a larger amount of electron production in order to have a charge balance because cathodic reaction is taking place this one and that is taking over the entire surface, and the amount of charge that is required would be greatly increased since the cathodic area is more.

Now the current if you consider the current that is flowing through the system is I now what would be my Ic. So Ic would be Ic-Ac which is the cathodic area which is nothing but the copper let me put copper and now if you consider the anodic area which is nothing but Ia by Aa. Ia is basically the anodic current which is same as the current that is flowing in the circuit. Now this Ia is a very small quantity because it's a rivet. It's a small section which is exposed. Now what would be my then ia? This is my ia which is nothing but the current density for the anodic reaction and here it is ic, minus ic. Now what would be the values? If you compare the values magnitude of this ia and ic since there is this Ic I copper, A copper is very very large that the area copper surface area of the copper surface is very very large and this area is very very small. So this would be very very large compared to ic if you compare the magnitude. So what do you mean by ia? ia is the rate at which anodic reaction is taking place. So this reaction is taking place. So if ia is small ia is very very large compared to the current density on the cathodic surface then the corrosion rate of iron would be enhanced to a great extent. So now you understand what is the importance of current density.

Now we have started with exchange current density. Now before going into the next section how to express the exchange current density with respect to the activation energy for metal ion formation. So before that let me see what are the factors that can affect i0. The factors are electrode material. Let's say for the same reaction hydrogen evolution reaction H+ for this reaction if you would like to consider what would be the value on platinum surface or on zinc surface you will see that the i0 value of this reaction. So we write it like this i0 H+H2 this i0 of this reaction on platinum surface so I am writing in the bracket the metal surface it means that on that surface this reaction is happening. So on the platinum surface would be equal to generally this value in case of acidic media it value goes to around 10 to the power -2 to 10 to the power -3 ampere per centimeter square. Same reaction.

Now if this reaction is considered in case of zinc surface then this value goes to 10 to the power -10 to 10 to the power -11 ampere per centimeter square. So you see same reaction you just changed the electrode material you are having huge difference in the current density or the exchange current density. Now what does it mean? If you have a very very high exchange current density because you considered that on the platinum surface i0 for hydrogen evolution is very very large that means that the rate, the quickness of attaining a reversible condition, quickness in attaining the reversible condition because i0 is nothing but the rate of evolution, hydrogen evolution, or hydrogen ion formation irreversible condition and if you have a very very large value that means that it's the equilibrium is attaining at a very very first rate or the advantage of having platinum it means that let's say you disturb this equilibrium, if you disturb this equilibrium by some means then if it is a platinum electrode then the equilibrium again will be attained quickly. So that would be very much helpful. You will see that later on what is the effect of this different i0 values. So this is the effect of electrode material.

Same way you can have difference in i0 value of the same reaction if you are using acidic media or basic media. So second case I am just noting all the conditions or the factors that would affect i0 values for a particular reaction then surface condition you know that we can have a platinum electrode or platinized platinum electrode. Now if you compare these two surfaces the platinized platinum electrode the exchange current density of hydrogen evolution is much more than that on platinum surface. So these two surfaces if you consider platinum and platinized platinum electrode these two surface condition are different. On the platinum electrode, platina pretty platinum electrode you have the platinum particles which are deposited on the platinum surface so you have a much more actual surface areas and that actual surface area will actually affect the exchange current density for this reaction.

Now third is the solution. You will see that if you are considering acidic media, if you are considering basic media this for the same reaction the exchange current density would be different. Then fourth is environmental condition. Let's say you are considering in case you are considering a dry – you are considering an area where you have much more presence of salt in the atmosphere or in the area where you don't have much presence of salt in the atmosphere. Let's say you are considering one section let's say you are doing some testing Visakhapatnam, Vizag or you are doing some test which is a sea region and if you are doing some tests in the Ladakh region you will have a difference in i0 values. Then five, temperature definitely. Temperature will definitely affect the i0 because the reaction rate it considered, i0 is nothing but the reaction rate or exchange current exchange current density is nothing but the reaction rate in the reversible condition. So the rate of the reaction always will be affected by the temperature.

Then you have surface roughness. So surface roughness actually this relates to this okay. So it's nothing but the same thing so let me remove this. So these are the factors which can affect the exchange current density. There are other factors. These are the main factors. Now let me now take let me now consider how to have a relation between i0 and the activation energy for ion formation. Now when you are considering this process it's not happening like that way that metal is immediately forming metal ion from metal ion or metal is immediately forming metal. In fact these metal ion and metal when they are crossing from metal to metal ion or metal ion to metal they are crossing a energy barrier.

Now if you consider this is my metal surface and this is my iron surface, n+ and M now it's not happening like this. Simply it's not going like this or simply it's not coming back like this. If you would like to find out what is the energy situation at these two sections then you will see that if you consider this is my free energy or G axis and if it's my reaction coordinate R/C or it's basically nothing but a distance, this is the distance and when it is at equilibrium, that case, these two sections are at low energy level and those will remain in the energy well and there would be a energy barrier which is nothing but delG star. I am putting it as delG star because this is nothing but the difference. This is let's say G1 this is G2 so this is the difference, difference is nothing but the delG star. I am just putting as delG star.

So now for this case and mind it this is – there is an existence of equilibrium. In that case I can find out what would be my flux from this section to this section and flux of metal ion to this metal surface because that equilibrium is existing, so rate at which let's see if it is rate 1 and this is rate 2 so rate at which metal ion is forming and the rate at which metal ion is depositing on the metal surface both are same so that rate can be expressed in the form of flux. The flux of metal I can put it as mole per centimeter square per second. I can express this in the form of this equation in n1 nu1 f1 exponential minus delG star by RT. Flux of metal going to form metal ion. What is the n1? n1 is moles per unit area in a favorable position that this n1 is the number of moles per unit area on this surface which are in a favorable condition to go from this to this. We are not sure that whether n1 entire n1 will go to that other side or not. That would be decided by f1. f1 is the fraction of atom or fraction of moles actually going from this to this and what is my v1, v1 is the frequency at which the mean frequency at which the metal atoms are vibrating. So this is around 10 to the power 13 per second.

So this is my flux from this to this. I can also write the flux of metal n+which is going to this. So I can write that as let me remove this part. I can write the flux of metal ion, again it's in moles per centimeter square per second. It can be written as n2 v2 f2 exponential minus delG star by RT and since there is an activation barrier and this is a thermally activated process, I can express the form of the flux I can express in the form of Arrhenius equation.

Now you see that at equilibrium the flux of metal ion that is going to metal this should be equal to this because this is nothing but the rate this is nothing but the rate and we know that at equilibrium r1 equal to r2 and I can put it as this one is r1 and this is r2. So r1 equal to r2 and we know that this delG star in both the cases these terms are coming, this exponential term both will get canceled if you have this equation then you will see that n1 v1 f1 equal to n2 v2 f2. Now this n2 is basically the number of moles per unit area on this section. So we have an important relation that this is both are equal.

Now generally this n1 v1 and f1, f1 is considered to be 1 if you think that all the metal what is coming on this surface that are getting accommodated on this section and the same way the number of metal ions which is going to this metal surface because of reduction process are getting accommodated on this surface. So if A1 equal to f2 it could be 1, and n1 and n2 since these are at equilibrium so this would also not vary and v1 generally both the cases it is close to 10 to power 13 per second. So if this term I can write in the form of a constant. Let me stop here.

Acknowledgment

Ministry of Human Resource & Development

Prof. Phalguni Gupta

Co-orindator, NPTEL IIT Kanpur

Prof. Satyaki Roy

CO Co-ordinator, NPTEL, IIT Kanpur

Camera

Ram Chandra

Dilip Tripathi

Padam Shukla

Manjor Shirvastava

Sanjay Mishra

Editing

Ashish Singh
Badal Pradhan
Tapobrata Das
Shubham Rawat
Shikha Gupta
K.K Mishra
Jai Singh
Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

Light & Sound
Sharwan
Hari Ram

Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh
Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla
Direction
Sanjay Pal

Production Manager
Bharat Lal
an IIT Kanpur Production