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Course Title

Environmental Degradation of Materials

Lecture – 26
Broad Subject: Crevice corrosion, Pitting corrosion

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So we see there are four stages for the crevice corrosion to occur, and the first stage it says that, so there will be if you have this crevice, this is let us say the crevice part, this is the crevice part now the first stage would be everywhere you have cathodic as well as anodic reactions, so stage one, everywhere you have cathodic and anodic reaction, this is also metal object, this is also metal object. And now inside the crevice you have metal dissolution, metal dissolution and this electron let me extend this part a little bit, so this electron what would be released by this metal ion, so here oxygen would come and leads to OH- formation, the cathodic reaction is happening here at the same time in the beginning you have the same cathodic reaction also would be taking place because initially the dissolved oxygen in the solution will be same, the concentration of dissolved oxygen in the solution would be same, in this place as well as the bulk of the solution. So here also you have oxygen coming up and taking care of this two electron another two electron is coming up, okay, so another oxygen is going and then leading to OH- formation, so like that you have more and more M2 + ion formation and oxygen is coming and taking care of that electron and getting to OHR - ion formation.

And also it is not like that only the metal dissolution is taking place in this zone, this is also taking place here also and this electron is coming and oxygen is taking care of that two electron and then forming OH – ion formation, so the anodic reaction is M2+ and cathodic reaction if we consider neutral seawater solution then we have + 2H2o + 4e going to 4OH – ion formation.

Now we see, as we have this more or less general corrosion tendency of metal and general cathodic reaction of this nature, gradually we see that the oxygen ion concentration in this zone is gradually depleting, why it's depleting? Because this gap one particular condition for crevice corrosion to occur, this gap should be wider enough to have solution ingress at the same time it should be narrow enough so that there should not be any turbulence, it should be stagnant in nature, so since this is stagnant and we have all those cathodic reactions gradually the oxygen what is there inside this crevice part that the dissolve oxygen content will go down, and if dissolve oxygen content goes down in this zone then we have preferentially the metal ion concentration gradually would increase and the other part which have lot of dissolve oxygen and other part there will be turbulence and the stagnant condition is here only, so the gradually the situation will arise that these part, these part which is inside the crevice will preferentially act as anode, the rest of the part which is in contact with the bulks of the solution that part preferentially this oxygen, oxygen reduction would take place, and OH- formation will take place. So gradually this part would be preferentially anode, and this part a bulk of the solution part would be preferentially cathode.

Now once we have this situation we have unfavorable area ratio also that particular condition is setting up, why? This crevice part would be a small friction but the bulk of the solution, the metal which is in contact with the bulk of the solution that has a huge area, so you have large cathodic area and small anodic area, so that would also increase the rate of metal ion formation or the anodic reaction in this zone, so gradually that this part is getting corroded.

Now once we have this metal ion formation in this zone, more and more metal ion formation is taking place, metal ion formation is taking place, so gradually you will see that this section we have excess M2 + ion, excess M2 + ion, that means this part is becoming more and more electro positive in nature and the system will try to neutralize this M2+ and for neutralizing this M2+ we need negatively charged ions, and who will supply negatively charged ions? So of course there will be OH- also would be existing there and as well as since the solution is NACL normal seawater, so the sea water we have chlorine ion, and the chlorine ion will try to migrate to this crevice part. And now we can have two stages reaction, first stages this reaction is happening and then gradually we have this depleted oxygen zone and in the crevice part and this more and more metal ion formation and unfavorable area factor that is also coming in.

Now in the stage two we need to neutralize, the system will try to neutralize this M2+, now who will neutralize? One way to neutralize this condition is M2+ we'll try to react with H2o and hydrolyze, so hydrolyze M(OH)2 this would form + H+ ion will form, now you will see if it is hydrolysis this metal ion then this hydroxide is forming and depending on the solubility of this hydroxide or the solubility product of this hydroxide metal ion concentration would try to exceed its value in this range, so if let us say if the metal ion concentration is such that it is lower than the required amount to form this, so this reaction would happen and this will form and if the solubility product of this metal hydroxide exceeds beyond that level metal ion, excess metal ion would be there here in this zone. Now the second part, this is first reaction that can be possible in order to take care of this metal ion and still if the solubility product increases then metal ion formation, steel would be there so further metal ion formation would be there if the solubility product increases, solubility product exceeds.

Now second stage is Cl - ion also tries to come here and try to, so more and more chlorine ion would come and this chlorine ion would react with M+2, try to form M Cl2, and this is another salt and this salt again would like to hydrolyze in the presence of water it will form M(OH)2 and + 2H+, so and Cl -, so let me combine these two, so this is an acid which is forming HCL acid is forming and then of course we have hydroxide formation again. Now you see that in this case, the product is H+, in this case also the product is H+ so that means gradually we increase the H+ ion concentration in this crevice part and log of H+ ion is negative of, this is nothing but the pH, so if we increase the hydrogen ion concentration the pH level in this crevice part increases and if it increases that means initially it was neutral, the pH level was neutral that means the pH was 7, now as we have these reactions the pH goes down and it can go to 2 to 3 level, so that means it becomes highly acidic in nature this level, and if this level goes into the highly acidic level and if it is a passivating metal then what would happen? Now we see according to the Pourbaix diagram, most of the Pourbaix diagram we see for example in case of iron we see that this is potential versus pH, in case of iron we see that, if as we, this is passive level, passive this is active, and this is a only metal ion or only metal, elemental metal is there non-corroding system, non corroding case, so now as we have seen that if I am maintaining my position at this point which is let us say close to 7, now as we go towards 2 to 3 pH I am here, so I am in the active zone that means the corrosion zone. So the same thing happens here if I go to the lower pH value so I increase the level of, I increase, I have the condition where the corrosion would be more compared to where I was in the beginning, so I increase the corrosion. At the same time since if it is a passivating metal then if we have the chlorine ion concentration in this zone, so if we have the more and more chlorine ion concentration sees the chlorine ion concentration increases that time chlorine ion tries to break down the passive layer, so that means two phenomena, one is, now in the third stage this stage is basically the second stage where I have increase in acidity or the pH value at the same time I have the increase in chlorine ion concentration.

In the third stage we have breakdown of passive layer and this breakdown of the passive layer this is enhanced because of the pH level 2 to 3 which is a much lower pH level or highly acidic condition as well as the presence of chlorine. So now if we combine all those three stages that means I have initiation of concentration cell that means here we have more dissolve oxygen here we have less dissolve oxygen and this becomes preferentially anode and this becomes preferentially cathode more and more metal dissolution metal ion dissolution and this metal ion since the metal ion concentration positive ion concentration is increasing so this metal ion will try to hydrolyze in the presence of H2o and tries to form H+, same case would happen the chlorine ion will try to come here and then tries to neutralize M2+ which is excess positive charge and this metal chloride salt will form, and metal chloride salt will again hydrolyze and form H+ and Cl- so we increase the hydrogen ion concentration or decrease the pH, and at the same time we increase chlorine ion and finally we have breakdown of the passive film. So you see that once we have reached to this level more and more dissolution will go on and finally at the fourth stage we will see that since we have greater amount of dissolution is taking place, finally if the cross section thickness is this, finally the system will have perforation, so finally the system will perforation or leakage would form. So this is the end of crevice corrosion, so that means at that point the entire structure is going to be crumbled and this structure will fail. So there are four stages, stage 1, stage 2, stage 3 and stage 4, and here the crevice corrosion stops, it doesn’t stop actually because there is no point in having this corrosion because the entire system will fail, so this is the entire picture of crevice corrosion. And also you see that this when it reaches to this level it becomes autocatalytic in nature, why? Because more and more, once these two reactions are starting up that time as we have this hydroxide formation this will try to settle down and we have increased H+ ion concentration as well as chlorine ion concentration would increase, pH goes down, chlorine ion and H+ acidic condition tries to break down the passive film gradually this entire thing keep on going on simultaneously and gives rise to enhance attack in this zone, so this is the mechanism of crevice corrosion.

Now let us see how we can have protection against this crevice corrosion, so preventive measures, first thing is we need to see that there is less creation of crevice portion in the structure, for example you have a lap joint, let us say this is my lap joint and the welding is done here. Now in case of lap joint there is a chance of formation of crevice, so instead of having lap joint we go for butt joint. So now we have welding at this point, so the bars, lap joint there is a tendency of formation of crevice in this zone so it is better to go for butt joint, so this is not good for crevice point, this is good for crevice point, so we avoid crevice formation. So we need to see wherever we find a way out we can go for that measure first. Now another example is let us say I have sharp corner in a water tank, now this is my position for crevice attack so if we can make it round shape pit, instead of sub corner if we make it round shape pit so I can avoid crevice and we can also avoid a position, at this position we avoid the stagnancy of the solution, so that means I can make suitable design so that we can avoid crevice corrosion or the crevice portion or crevice part of a particular structure.

Another example is let us say we have, say this is one bold joint and let us say we use a rubber gasket here, let's say this is a rubber gasket now if we use long rubber gasket and the gasket becomes so long that it takes the shape like this and this becomes very deadly combination, why? Because if this is my rubber gasket, now this is crevice so this part and this is an example of crevice between nonmetallic object and metallic object, this is my metallic object and this is my nonmetal so this is a crevice part where I have the condition for crevice and crevice corrosion can happen, so that means the first stage is we have to avoid crevice formation, wherever possible and that crevice formation can be avoided by choosing suitable joining mechanism instead of lap joint we can go for butt joint, instead of having a sub corner in the water tank we can have a rounded corner, or in this case how we can avoid it so we have to cut this part, if we cut this part so that means I avoid the crevice formation, so this is another mechanism by which we can avoid crevice attack, so avoid crevice formation.

Now second case is proper design, proper design for example this is a design criteria making the rounded bottom and let us say I am holding it like this, I have a bottom which is cemented bottom, this is my cemented bottom and this holds this entire rub metallic structure so that case this is also not good design because this is another crevice, crevice means a sub corner, so how to avoid it? So we can avoid it by suitably changing this part we can make it like this, like this we can make so I am avoiding sub corners, so proper design is another tool, and then third is avoid time to time, timely cleaning. Timely cleaning what does it mean? Now let us say I have a dirt particle like this if the dirt particle is there so I have crevice formation here, this is the crevice so this zone will be corroded. So if we have some arrangement so that the water waste, whatever water is going inside that water is filtered so the dust particle is not allowed to go into the storage tank so that would be better, so timely cleaning or if it goes there so time to time we clean the bottom part, if the bottom part is clean so we take care of this dirt particle then we can avoid those crevice attack, so these are a common examples of preventive measures so we can take care of the crevice corrosion if we follow this kind of situations, this kind of measures.

Now once we see the crevice corrosion then there is one more localized attack and that is a very, very deadly attack if we consider all the forms of corrosion that is pitting corrosion.

So now let us get into the pitting corrosion part, now in case of crevice corrosion we see that we have a sharp crevice, this is a crevice part where I can have localized attacked and there I can see that the attack is very localized and other part is getting protected but this part we can have a sharp group like this. Now in case of pitting this is also highly localized attack, highly localized corrosion and there on the flat surface even if we do not have crevice on the flat surface we can see that at localized position the attack could be such a sharp group sort of attack that can happen. And the most important part here is why it is so deadly that when we have such kind of attackers mascha group, micro dimension group that is forming and it is going down, now if we consider the amount of metal loss if we see the amount of metal loss in this case it would be a miniscule loss very, very small loss, very, very small loss so if we measure the wet so it does not give you that much of corrosion it is a very, very small amount but the point is the attack is highly localized and it has formed a group and it may happen let us say this is my cross section now if it is under stress, tensile stress the cross section is decreasing and at the same time the sharp nature of the pit, this is called pit sharp nature of the pit will try to break the sample and of course it breaks without giving any indication it breaks and that is a catastrophe, it is a severe failure that can happen and it does not give any indication and the loss of material would be so low that nobody would understand that how much corrosion had happened, so the pitting corrosion we have to again look into more carefully now if we see the definition of pitting corrosion, if we see the definition of pitting corrosion it is extremely localized corrosion and it happens in small areas.

Now, why the small area? Because if you see this entire structure entire cross-section let us say this is the big cross section like this, now in this cross section only a small part is getting attacked and the attack is in the thickness direction of the particular structure, now this is extremely localized and it forms cavities or pits, so the cavities or pits that are there, now once we have this definition then we have to see what are some of the characteristics of pitting, if you would like to get into the characteristics of pitting, now one is it generally happens for the metal which are passivating in nature, so passivating metal for example aluminum, steel, they are prone to this pitting, and this is very insidious form of corrosion, some of the characteristics, and third one is it doesn't involve much of weight loss, and of course if you would like to measure what is the pitting corrosion rate that time we should measure in terms of mils per year or millimeter per year, and here this is called MPY and this is called MMPY, this is milli inch per year and it talks about the depth measurement of the how far it has gone through the depth direction or the thickness direction. And the formula would be I which is the ICorr, A is nothing but the atomic number of the particular metal or equivalent atomic number for the particular alloy and the Rho which is the density or equivalent density of that particular alloy, if 1 Faraday and the number of electrons that is involved, so if you have this formula then we can measure what is my millimeter means penetration per year, or millimeter penetration per year, this is the way we measure what is the my pitting rate for the particular metals or alloys, so these are some characteristics.

Now let us get into what are the factors that lead to pitting corrosion. Factors, first factor is surface defect, what are the surface defects? Surface defects, for example this is my surface, this surface let us consider this surface, this surface, we have grain boundaries and let me remove the background part. Now if you consider this surface we have different grain boundaries and now also we have triple points and those triple points are highly energetic and if we have some chemicals on top of it then this triple points are the first positions or the first, this triple points will get attacked and there would be a tendency of pitting formation.

Now in the metal also we have different inclusions and mainly manganese sulphur, for example in case of iron we can have sulphide inclusions and mainly in the form of MNS, and the MNS is highly detrimental to the metal or iron, if you have a small metal ion MNS concentration this is, let us MNS inclusion and those inclusions there is a possibility of pit formation.

Now another case is what are the other defects? For example there could be inhomogeneity in the composition, inhomogeneous concentration for example some part will be enriched with some particular elements that are the places where we can have pitting, the surface defects are detrimental, and surface defects are, on the surface defects we can have pit formation.

Second example, degree of cold work, this is also a very major factor which lead to pitting, for example one example that severe cold work in case of austenitic steel, in case of austenitic steel if we have severe cold work and if it is exposed to ferric chloride then there could be pit formation. Now there could be on another factor, third factor surface finish, surface finish generally we see that if a metal surface is highly polished with very little presence of scratches those metal surfaces are having a very high resistance to pit formation, okay, so surface finish if it is highly polished at the same time less of scratches we have a better pitting resistance, but another important issue with the surface finishes and if the surface finish is less rough and highly polished and if there is any pit formation, let us say here we have a pit formation and that pit has a tendency to go deep into the middle and that pit becomes very, very large, very, very wide pit it can form, but the number of pits would be less, but if there is a bit formation that pit can go deep into the middle the surface finish is one of the factor.

Now fourth factor is sensitization, sensitization temperature, so we see there is one more factor that is sensitization temperature, the sensitization part will discuss more when we discuss intergranular corrosion and in case of 18:8 stainless steel, 18:8 stainless steel generally we come across the sensitization effect which is nothing but formation of chromium carbide along the grain boundary so we have let us say this is my stainless steel and this is my grain boundaries, the chromium carbide generally tries to form along the grain boundaries so these are chromium carbide, these are chromium carbide so once we have chromium carbide formation along the grain boundary zone then the surrounding region, near that grain boundary part is depleted with chromium, and in case of 18:8 stainless steel we have 18 waitperson chromium and this is stainless because we have very high amount of chromium, at that chromium forms chromium oxide on the surface of the stainless steel and that gives you stainless property.

Now if you have a depleted chromium around that grain boundary so that part will be active in nature and since the body part away from this part has this 18% chromium only that this narrow part is highly depleted with chromium, so this part will act as anode surrounding part will act as cathode, and then we have the situation of unfavorable area condition where large cathode and small anode, so the corrosion will be concentrated near this grain boundary zone and finally the failure can happen around this, along this grain boundary, so this happens, this chromium carbide formation along the grain boundaries in the stainless steel this happens in a particular temperature zone, and in that zone generally that is 600 degree Celsius to 400 degree Celsius in this temperature range when it is cooled in this temperature range slowly then chromium carbide nucleation can happen along the grain boundary, so if it happens then there the condition becomes sensitization, that particular situation is called sensitization and we say that the 18:8 stainless steel has become sensitized because of the formation of chromium carbide along the grain boundaries when it cool slowly in this temperature zone, and these temperature zone is called sensitization temperature, fine. So if we have this situation, chromium carbide depletion along the grain boundary as well as chromium carbide formation along the grain boundary then we increase the tendency for pitting along the grain boundary, so somehow we have to avoid this sensitization temperature zone where we should cool it rapidly in order to avoid chromium carbide formation, so this is one factor.

Now another factor is environmental contamination, environmental contamination it combines the crevice and pitting together, why? Let us say I have a bottom of water tank, I have big dirt, dirt particle and we have a crevice formation and these zones is basically highly susceptible to pitting, now that means pitting and crevice those are very closely related. Now another point I would like to mention that wherever you have crevice there is a tendency of pit formation, but other way around is not true, for example on a flat surface you can have pitting, at the same time in a crevice part you can have pitting, so that means crevice is always associated with pitting, but pitting may not be associated with the crevice, so that is important observation since we can also have pitting on a flat surface.

Now environmental contamination means all those dirts even biofoulings, this is biofoulings deposition this happens in case of seawater corrosion of ships so there if we have this situation or sort of crevice formation then we can have pitting related corrosion process, so the environmental contamination we have to avoid this sort of contamination so the same protection mechanism what this applies in case of crevice and this also applies in case of pitting so if we avoid this environmental contamination we can avoid pitting corrosion.

Now six point is of course composition, composition of metal and alloys those are very important issue, for example in this sensitization cases so we see that chromium carbide is forming along the grain boundary so we have compositional homogeneity somehow if we can avoid this chromium carbide formation on the grain boundary we can have a very good stainless property, stainless means there is no rust formation and it becomes shinny all the time, now this chromium is the main allowing elements which leads to stainless property so we have to make sure that chromium always stays in the solution and it is uniformly distributed over the entire structure, so the composition that means the chromium presence is important parameter in case of stainless steel also this chromium if we add little bit in magnesium, aluminum magnesium alloy or aluminium magnesium zinc zirconium alloy if we add chromium little bit we can get very good pitting resistance, so pitting resistance is possible. So alloying element can lead to huge difference in the pitting resistance, for example in case of 18:8 stainless steel if we add molybdenum in it, so if we when we add molybdenum in it we can get very good pitting resistance what molybdenum does? It just helps in making the passive film more stable and if it becomes more stable so pitting attack would be less, so molybdenum addition in 18:8 stainless steel, okay, so we can get very good pitting resistance, the composition is another important parameter.

Now we have one another important parameter that is velocity, velocity of the solution is very important now we have example for that, for example if we consider the velocity part let us say stainless austenitic this stainless steel pump, stainless steel pump if it operates continuously and it deals with seawater, if it continuously operates and it is dealing with seawater we don't get much a problem with the pitting. Now if it stops and stays idle then there could be a serious problem with pitting, so and why, when we come to the mechanism of pitting we will see that these also associated with the stagnancy of the solution, stagnancy of the solution, so when it is not operating, when it is not rotating that time that a water becomes stagnant, and if it becomes stagnant then this stainless steel pump might fail because of pitting.

So let us say if we are going for some maintenance then it is advisable that time to time we operate this pump. let us say for 2 minutes or 3 minutes just to have, avoid this stagnant solution condition so the velocity is another important parameter and we can do one small experiment let us say one there are 3 beakers, the same material let us say same stainless steel, same stainless steel is put in that solution of NACL solution or seawater solution, and one case it is stagnant completely stationary, one case it is moving at a slow speed this water is, there is turbulence and the relative movement across on the metal surface let us say that speed is very small. And if we have a severe turbulence in this water severe turbulence then after some time if we take the sample out we will see that this case has the maximum number of bits and this case has the minimum number of bits and the high speed of the solution or the electrolyte also tries to maintain uniform oxygen distribution over the entire surface and it tries to make the surface layer or the passive layer uniform throughout the section, so it helps in high velocity helps in maintaining the passivity at the same time it tries to protect the surface from pitting, so these are the major factors which governed, which tries to affect pitting corrosion.

Now let us come to the condition when the pitting can occur. Condition for pitting, one is breaks in the film, this film is nothing but the passive film, breaks in the passive film and this can happen due to lack of homogeneity and this homogeneity it could be chemical composition, there could be formation of, there could be a chance of having inclusion this can happen due to this or this can happen due to water or the solution ionic concentration. Let us say some part is highly rich in dissolved oxygen, some part is depleted with dissolve oxygen say then we can have a different aerated and differential aeration, aerated cell and that can lead to pitting.

Now second condition presence of halogen like Amazon halogen ions chlorine - chromium minus - fluoride ions, so fluoride salts all those can lead to pitting, serious pitting.

Now third is stagnancy of electrolyte and this stagnancy can seriously happen in case of crevice, it can also happen on a flat surface, on a flat surface let us say momentarily there is some rapid dissolution and if momentarily there is a rapid dissolution in this part so in this section the solution can become stagnant and this momentary dissolution or rapid dissolution can happen near the grain boundary region, let us say this is my grain boundary, this one grain boundary is combining or with this dissolution process or there could be a formation of, there could be inclusion, there could be inclusions and that inclusion can lead to localized attack or in case of sensitized condition the formation of chromium carbide along the grain boundary and leading to chromium depletion near the grain boundary and that chromium depleted zone can have rapid dissolution, and once we have a groove formation let us say this groove has formed and even here also this groove has formed, see if we have a groove formation like this in the groove there could be stagnancy of the solution, and once we have stagnant solution we will see that the situation becomes same as the crevice corrosion so we need to see the mechanism of pitting corrosion, so the mechanism of pitting corrosion we see that we will find that is almost similar like crevice corrosion, so mechanism almost similar like crevice corrosion and let us discuss this mechanism part now.

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