Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 27
Broad Subject: Pitting corrosion, Intergranular corrosion

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So we see that there are three major conditions in order to get pitting, one is brakes in the films or there could be other defects such as lack of homogeneity in the film, then presence of halogen ions, chloride, bromide, iodide, fluoride and stagnant service condition, and also we need to have a particular surface condition, for example if there are some inclusions which is on the surface or if there are sensitized condition all the things we have already seen.

Now let us get into the mechanism of pitting, if we see the mechanism of pitting there are three stages for a pitting to occur, one is initiation, initiation of pit and second is propagation, propagation of pit and at this condition we have autocatalytic nature, and then third stage is basically the perforation or pitting termination, it's actually can lead to leakage, so this are the three stages of pitting formation. And let us get into the different processes that are going on during this three stages, if you consider the initiation of pit actually on a surface you have let’s say you have dissolved oxygen and that too in sodium chloride solution and then and if the metal is passivating in nature so let us consider this three conditions, one is seawater, second is dissolved oxygen presence, third is let’s say it's a passivating metal, this can also happen in case of non-passivating metal, but we generally come across this pitting very often and severely in case of passivating metal.

Now let’s say on the surface you have, let's say this is my surface you have lot of grain boundaries, lot of grain boundaries as well as there are many inclusions, these are the, some of the inclusions or it may happen, let’s say in case of sensitized stainless steel there could be development of depleted grain boundary zones, depleted grain boundary zones and these are basically depleted grain boundary zone GBZ, GBZ means grain boundary zone, so there we have little higher tendency for dissolution, so initially dissolution would happen all throughout this, just a minute, we’ll stop for a while, so that means we have some of the sections on the surface of a particular metal when is this exposed to seawater with dissolve oxygen, now there are some places, for example inclusion zones or grain boundary zones, there are some of the areas where we have higher energy compared to the bulk of the system, so initially if it is exposed to this solution there could be cathodic reaction, the cathodic reaction is of course we know this would be cathodic reaction, and the anodic reaction would be M going to M2+, so this is my anodic, and this is my cathodic, this is my cathodic reaction, so all throughout the surface this two reactions are happening, and initially the metal is going under uniform attack, but since we have some of the zones which are high energy zones there could be a momentarily, there could be a huge rate of corrosion at some particular section or particular point or particular region.

Now let’s say at some moment there is a section where you have extra dissolution, so let’s say this is my cross-section and this is my if I am seeing through this thickness direction so I see that there is a little bit of extra dissolution momentarily and this is the start of the pitting of the initiation of pitting, that means and of course the solution is stagnant in nature so pit forms, now once we have this pit form let us look into this part and zoom this part what happens at this zone, so we have this zone, so still we see that metal ion is forming, so metal ion is forming and of course this metal ion would be consumed by this electron what are released by this anodic reaction they will be consumed by let’s say this electrons are going, okay, so electrons are going from several position to several sites, okay, so electrons are coming like this, here also electrons are going so oxygen would come and it forms OH- ion, so here also oxygen is coming and it is forming OH – ion and this side also the same story. So these electrons are basically consumed by dissolved oxygen and it takes, it goes for this cathodic reaction and it forms OH-ion.

Now the situation is gradually changing, the situation is changing in such a fashion that you see since it's dissolved oxygen and since initially all throughout the cathodic reaction is taking place in this section we have more and more stagnant condition and this looks like a section similar to pitting, a similar to crevice where we have a very small section where we have a very much stagnancy in the solution, so since this section is stagnant and the other section still little bit of a movement could be possible, but still this overall solution is more or less stagnant but this section would be much more stagnant compared to the other section so since oxygen is taking care of this electron so in this part gradually we will see that the oxygen depletion will take place, oxygen depletion is taking place and since this is stagnant so oxygen is gradually coming inside but since the stagnancy is maintained so oxygen coming from the bulk of the solution to this section would be less, so we have less of oxygen in this part, more oxygen in this section.

So now we have the peculiar situation and this situation is related to a sort of concentration cell, now since we have low oxygen here and we have high oxygen here so the high oxygen part will be cathodic, so this part will be anodic, and this part will be cathodic, why? Because we know that from this if you see this reaction we can write it in terms of potential E0 which is standard reduction potential + RT 4e, 4 electron, that means 4F Ln Po2 H2o (Oh)4, so this is my equation. Now if you have a less dissolved oxygen here so the Po2 in this case would be less, and Po2 in this case would be high, so that means in this case let me consider their potential E2, and in this case the potential is E1, so the E1 would be higher than E2, so we have E2 and E1 zone, so since E1 in the reduction potential that is E1 is higher or the value of E1 would be more larger than this, so this will act as cathode and this will act as anode, and this part will have anodic zone, and this part will have cathodic zone. And now see that we have differential aeration cell or concentration cell and the largest section of the surface are cathode, and of course that larger section are more or less cathodically protected, but the anodic part will have a small area and the large cathodic area so the unfavorable area ratio, so more and more anodic dissolution would take place in this zone.

So if more and more anodic dissolution take place in this zone, so gradually we will see that this section we have higher metal ion concentration, now if there is higher metal ion concentration so it is act, it is acting like a electro positive section so the system will try to neutralize this situation, so who will neutralize? Since we have sodium chloride, so the chloride ion will try to come, will try to come in this zone, so if chloride ion comes to this section now there, two reactions that are possible, one is metal ion and it will react with H_2o, metal ion would hydrolyze and it will form $M(OH)_2 + H^+$, if we make it 2, so $2H^+$, this would be 2 then, just a minute, we have to balance this, how we could balance it? So OH + H, so now if we make it 2, so this is balanced now, now we have 2H + ion in this section, so we see that and this is of course a metal hydroxide which would deposit and depending on the solubility of this metal hydroxide until and unless the solubility of the metal hydroxide at the service temperature is not exceeding metal ion, whatever metal ion that is forming that will go into metal hydroxide, once the solubility of metal hydroxide would increase then the metal ion formation, metal ion formation in this section would increase, so once we have hydrolysis reaction so $2H^+$ ion formation would be there, similarly since chlorine ion is coming here the metal ion can combine with chlorine minus and then of course it can hydrolyze again and it can form metal hydroxide and HCL acid and of course this is the situation. Now this can also happen, now if this happens then we see that gradually the hydrogen ion concentration in this part is increasing so the first case is the initiation momentarily some section is dissolved quickly, and it forms a small pit, once pit forms stagnancy of the solution as well as oxygen depletion forms a concentration cell and then you have a differential area factor or unfavorable area ratio so this section would be preferentially going into the solution in the form of ions, these ions will combine with hydrolyze in the presence of water forms H^+ ion, and as well as chlorine ion would come here to neutralize all those extra positive charges and then that metal chloride, the salt what is forming there that would also hydrolyze and then form acid. And of course there would be chlorine ion concentration also.

So now once we have increase in hydrogen ion concentration as well as chlorine presence that chloride presence they will act adversely to the passivity, okay, so what would happen? So these two thing, this hydrogen ion that means if we increase the hydrogen ion concentration pH goes down, let's say initially the pH was 7, so pH can go to 2 to 3 so it becomes highly acidic, at the same time since chloride ion is there so they will act adversely to the passivity and there could be break in the passive layer, so break in the passive layer and as well as this situation, this situation is continuously running, so the situation become autocatalytic in nature, more and more metal and comes out, more and more chlorine ion goes in, more chlorine ions go in there would be hydrolyzation, or there will be hydrolysis and metal ion itself can hydrolyze so there will be increase in pH and chlorine ion presence break in the passive layer, so the passive layer will always be unstable in this zone and gradually this the thing become more and more aggravating in nature and dissolution would go in like this at a very, very fast rate. So this is the stage which is the second stage propagation of pit, which is autocatalytic in nature.

Now since we have, this is the thickness let’s say this is my thickness gradually this will grow and finally there would be through nature of the pit and the perforation would happen and the material will fail, so this is the mechanism of pit and you would see that there is a lot of similarity between pitting and crevice mechanism. So now we have to think of what could be the preventive mechanism, so if we see the preventive mechanism whatever we have thought about the crevice prevention those will apply here, so the whatever prevention mechanism we have for crevice that would active here, so one is all methods crevice corrosion, protection, processes or protection ways will also act as protective measures for pitting.

Second, this is protection, making the passive layer more strong, more adherent, more stable, so generally stainless steel if you consider stainless steel we add molybdenum, so if we add molybdenum the passive layer becomes more stable so making more stable. And now you see that if there is no stagnancy, now temporarily there is a small dip and the stagnancy of the solution tries to create this concentration cell, let's say there is no stagnancy so oxygen can easily get in here, okay so the cathodic reaction would also happen here and then gradually this will become, this small groove would go so the small groove will not be present anymore because the concentration of oxygen is maintained same throughout, there is no concentration cell because of movement in the solution, the stagnancy is one issue so somehow the material which will be used for some application let's say pump application that case it should be operated for continuously so that there will not be any stagnancy in the solution though avoidance stagnancy that’s what the pump, stainless steel pump that is to be operated time to time when the system is under maintenance in order to avoid this avoidance of, avoid this stagnancy case, so if there is stagnancy pitting can develop.

Then we have different alloys are there where we have increase in pitting resistance, for example if we consider the increase in pitting resistance bottom would come 304 stainless steel, then 316, then Hastelloy, Hastelloy then it can have titanium, so it is basically pit resistance increases as we go up like this, so depending on the situation or depending on a corrosiveness of the solution or the environment we can choose a particular metal and alloys. So these are some of the basic protection mechanism and now if we follow this kind of protection mechanism we can avoid pitting to a great extent, so this is about pitting.

Now let us get into another form of corrosion that is called intergranular corrosion, intergranular corrosion we'll look at it before that I missed the point, let’s say this concentration cell effect is active in case of pitting, now we have seen that in case of corrosion we have different forms, eight forms and there are different factors, one of the factors is concentration effect, now there we have concentration cell and we have seen that how the concentration cell is forming, now one major atmospheric corrosion is due to this formation of concentration cell that thing let us just discuss a little bit, if we see the rain water or rain droplet which is falling on metal surface let’s say mild steel and then we generally see that at the center of the droplet the corrosion is maximum, okay, so let’s say this is the flat surface of that mild steel and now we have a droplet, water droplet, I have made it bigger, made it big just zoomed it, so now if you see this droplet of course this droplet outside we have oxygen and this is in the normal environment, so in the droplet also we have dissolved oxygen, we have dissolved oxygen now once we have dissolved oxygen we have an electrolyte, this rain droplet will act as electrolyte and of course the metal dissolution can happen since this is mildly acidic so we can consider this reaction to be the cathodic reaction, this reaction we can consider to be the cathodic reaction, so this cathodic reaction can happen and since we have electrolyte, so this anodic reaction can happen, this is cathodic, this is anodic.

So now gradually this both the reaction are going on and this rainwater is almost stagnant in nature, so gradually the oxygen inside the part, inside section or the center part of this droplet so if we see from top you will see that this is my section, so this part we have depletion in oxygen content, so if you try to measure what is the oxygen content from the edge of the droplet to the center of the droplet so we can have a decreasing trend in the dissolved oxygen, so partial pressure of oxygen if you consider, so partial pressure of oxygen would be having a decreasing trend, so this way I have drawn it like straight line it may not be straight line but it would be having a decreasing trend and this is the zero distance, let's say this is my zero distance and this is the R, so this point is R so it has the lowest, the center would have the lowest oxygen content, once these two reactions are starting and gradually this oxygen level at the center would go down, but since this part which is in direct contact with atmosphere so oxygen can go in and then make out whatever depletion of oxygen is taking place, so we have higher oxygen content in this section, and in this section we have low oxygen, so same theory would work here, so low oxygen, high oxygen so this part would act as anode, and this part would act as cathode.

And this is a narrow section, this narrow section would be cathode and the rest of the section would be anode, this section would be anode and this arrest of the section would be cathode since we have a higher oxygen level, so now we have a differential aeration cell or concentration cell, concentration cell is basically with regard to oxygen so gradually we will see that dissolution pattern would be like this, so at the center part we have more and more dissolution compared to the periphery part of the water droplet or the rain droplet on a mild steel, so this is a classic example of concentration cell development and that consequence would be the corrosion at the center of the concentration, center of the rain droplet.

Let us get into the form which is intergranular corrosion, let us discuss intergranular corrosion, the intergranular corrosion the name suggests inter granular so that means between the grains or at the interface of the grains between two grains there the corrosion is happening so that's what this name is intergranular corrosion. Now if we see a microstructure, polycrystalline microstructure we have different grain boundaries and let's say it is being etched by a chemicals, so when it is being etched by a chemical that time the first place where the attack would happen that is basically the grain boundary zone, why? Because the grain boundary zone has a higher energy level and if we consider the energy criteria so G is nothing but -NFE so more would be G, less would be E, so I will see that this section would act as anodic zone, and the rest of the section where we do not have the grain boundary it will act as cathodic zone, so the attack would happen around this section.

Now let's say I would like to go for a higher more and more etching so that means I would like to over edge the surface, if we over edge the surface we will see that the etch pits are arriving, those etch bits are nothing but the dislocation surface interaction and the dislocation is basically penetrating the surface and the dislocation core has a higher energy, so those will be active after grain boundary attack so then that part will have a feature which is a dark feature which is called etch pit.

Now during over etching though we see the etch pit but we don't generally see that the grain boundary regions are attacked more and more, so the grain boundary regions of course they will be attacked, but the attack severity of the attack along the grain boundary will not be that, will not be that active or that exuberant in nature, so we see that though attack is taking place along the grain boundary region as well as active zones we don’t have much of very severe attack on the grain boundary, but the situation would be different if we somehow make the grain boundary zone very, very active due to three reasons, one is some element segregation, element segregation or enrichment with some element, second reason could be impurity content, higher impurity level along grain boundary, along the grain boundary and the third reason would be depletion of alloying elements. So we see some conditions because of this three effects enrichment of the grain boundary with some elements impurity increase, increase in impurity concentration along the grain boundary or depletion of some alloying elements those, these three conditions can lead to make the grain boundary so active the other part will be almost protected or very little corrosion would happen on the other section of the material except the grain boundary zone, and the grain boundary attack would be so severe that the material can fail because of this grain boundary attack.

Now this kind of preferential attack along the grain boundary is termed as intergranular corrosion, so if you want to, if you would like to see the corrosion grain boundary definition is basically the preferential attack along the grain boundary due to very, very active nature of grain boundary, so this grain boundary and this active nature of the grain boundary could be due to this three effects. Now let us see some of the examples of these three effects, three main criterias where we have this grain boundary attack, preferential attack, and the preferential attack means the rest of the part of the material will not get attacked much, only the grain boundary part will be attacked. Now one example with for this is in case of brass when it solidifies generally zinc goes to the grain boundary section and there could be increased zinc concentration along the grain boundary. So zinc segregation or enrichment in brass, this example is zinc enrichment in brass.

And second case, generally in case of aluminum alloys iron can go into solution with a very, very minor amount, now this iron if it is present in aluminum alloys this iron is considered as impurity in aluminum so that iron can also go to grain boundary regions and make the grain boundary very, very active. And the third example and this is the most well-known and well discussed example that is depletion of chromium in along the grain boundary, along the grain boundary in case of stainless steel and that to 18:8 stainless steel or 18:8 austenitic stainless steel. Now these are the common examples for all those three situations we will discuss more about this. Now when we discuss this we would come to know that why preferential attack is taking place, so let us see a particular 18:8 stainless steel, 18:8 stainless steel where 18% is chromium, 8% is nickel.

Now in case of stainless steel because of the presence of chromium in solute solution that means the chromium is in the substitutional position in case of stainless steel, so that content of chromium would be effective in forming of passive layer which is a chromium oxide nature and that chromium oxide would give the passivity and that is what the stainless steel does not get the stain, so it doesn't have the rust formation, so the chromium gives the stainless property to the stainless steel and generally around 10% to 12% chromium in solution that is needed in order to make the stainless steel to be stainless. Now if somehow the chromium level goes below around 2% to 3% or below 3 percent then the stainless would not be maintained, stainlessness would not be maintained.

Let’s say I have the grain boundary like this and in case of stainless steel we see the intergranular corrosion and let’s say when this stainless steel is exposed to some seawater or acid solution we have grain boundary attack, preferentially grain boundary attack is going on. Now if you see under microscope we will see that along the grain boundary regions we have small, small chromium carbide precipitates, these are all chromium carbide CR23 C6, this are the chromium carbides which are forming along the grain boundary. Now if you do composition analysis we will see that in this section the chromium content is still 18%, chromium content, but in this section chromium content can go to less than – 2, less than 2, so that means in the body part we have still 18% chromium which is the condition that is required for stainless steel property, stainless property that is 10% to 12% which is more than, this percentage is more than 10% to 12% chromium, but in this section this section except that chromium carbide part the surrounding regions of this chromium carbide part, the chromium content is less than 2%, so once it goes below 2% so we don’t have the protection which is to be given by the chromium in the form of chromium oxide. So this section there is a possibility of and of course the chromium carbide, chromium oxide layer forms on this section, this section also the chromium oxide forms, this section chromium oxide forms, and of course this contains lot of chromium, so around this it is not a problem so in this also act as cathodic, because since the chromium, this carbide phase is cathodic in nature compared to iron, but since we have a depletion of chromium that means it has gone from 18% to 2% or less than 2% this depletion will lead to form anodic zone in the depleted part. So this section would act as anode, the rest of the section would act as cathode and the chromium carbide also will act as cathode, so the depleted part will be anode, depleted part would be anode and the surrounding regions cathode, surrounding region would act as cathode.

Now you see that this anodic part is basically a very, very narrow region, and the carbides are forming along the grain boundary regions and the depletion is taking place along the grain boundary regions, so this is a very narrow section compared to the surrounding cathodic zones, so you have unfavorable area factor, so if we have unfavorable area factor so the dissolution along this zone would be very, very high because rest of the part is protected or very little corrosion because of this cathodic nature and this section is anodic at the same time this is a depleted, this is basically a small anodic area, so the corrosion rate along the depleted section would be many fold, so gradually the depletion this intergranular corrosion will get into the bulk of the system, and there could be failure. Let’s say if this is under tension, and the groove is forming, there will be groove formation like this see if you see the three dimensional nature along this if you see the groove is going inside the material and since this is a subgroup the material when it is pulled it will fail and there could be a possibility of intergranular fracture surface, intergranular fracture.

Now if you see further this picture the situation is like this, let's say I would like to see what is the depleted zone so if you see this is my carbide, chromium carbide, this is my chromium carbide and chromium concentration if you see from, this is my chromium concentration so along the carbide there is a huge increase, but as you go away from the carbide then you have gradually with the lowest amount of carbide, lowest amount of chromium, sorry it is basically the chromium content in this zone which is the grain boundary zone actually if I see this part and see along the thickness direction I can have a situation like this, so we see that this is the depleted chromium carbide zone, and these part corrosion would take place and finally we have corrosion attack along the grain boundary due to this effect and also unfavorable area factor. So this is the nature of intergranular attack in case of 18:8 stainless steel and the situation would happen if we have preferential formation of chromium carbide along the grain boundary zone.

Now when would there be a possibility of chromium carbide formation along this grain boundary in case of 18:8 stainless steel, so for that we need to satisfy few situation, one situation is the carbon content, if the carbon content is more than 0.02% then chromium carbide precipitation can be possible, so for that we need to see a phase diagram for stainless steel austenitic stainless steel and if we see the phase diagram, now this is phase diagram is basically nothing but the temperature and here its carbon concentration then if we see that we will see that the phase diagram is like this, and this is my gamma + carbide, and this section is nothing but this is, this temperature is around 600 degree Celsius, this is gamma + alpha + carbide, and this part is austenite.

Now in case of iron or in case of 18:8 stainless steel this is pseudo binary diagram, pseudo binary diagram means we have other alloying elements but actually we are not considering other alloying elements we are only considering temperature and carbon concentration and trying to see what is my different, what are the different phases that can arise during cooling. Now we are starting with this, carbon content is close to around 0.02 or less, this carbon level, now let's say I started with the carbon content around 0.08%, now when I cool it and this is the solidus line then if I come to this place so I will always see that this much carbon is excess, so this much carbon is basically, this much carbon is excess in the material so if we allow some time then this much carbon would try to come out from the lattice and try to form carbide, and since chromium has a very high affinity towards carbon and also the chromium content is very high in the 18:8 stainless steel which is around 18% so the chromium will react with this excess carbon will form carbide, and at the same time these carbide formation, chromium carbide formation is a nucleation and growth phenomena so they will try to form along the grain boundary, because the grain boundary will provide heterogeneous nucleation sites for carbide to form, so if the carbon content is more than 0.02% the carbide formation tendency is increasing, this is condition number one, so the carbon content.

Now the condition number two is, the condition number one is carbon content, condition number two is the temperature zone where we have long aging, if at a particular temperature zone we have a long time aging we can have carbide formation or chromium carbide formation along the grain boundary, we will see this chromium carbide formation due to aging in a greater depth and we will also see that because of that temperature and time condition we can have, we can also design the protection mechanism from this carbide related depletion and intergranular corrosion of austenitic stainless steel. Thank you.

Acknowledgement

Ministry of Human Resource and Development

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Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

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