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Course Title

Environmental Degradation of Materials

Lecture – 29
Broad Subject: Dealloying, Erosion Corrosion

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So you see dealloying or selective leaching that means that the noble metal stays and in the alloy active metal goes out in the solution, in the form of ions, so there are many variations, one particular variation is dezincification, so let us discuss dezincification, dezincification means zinc goes out in the form of ions from brass and copper stays back, and in that case if we see some of the characteristics of the dezincification of brass that time actually copper + zinc alloy, and in that alloy zinc goes out and copper stays back, so finally we will see that the surface is enriched with copper and depleted with zinc and the surface becomes porous in nature and the strength of the brass decreases, so if we see that it is observed in a naked eye and the surface become red in color compared to the original yellow colored brass, generally the yellow colored brass is 70: 30, 70:30 brass, where 70 weight percent of copper, and 30 weight percent of zinc that constitute the alloy brass.

Now this becomes red-colored from yellow color, due to dezincification and this red color because the copper enrichment happens on the surface, then there could be two types of Dezincification, one is layer type or plug type, so generally in case of pipeline made of brass handling portable water there we see that the inside surface uniformly that gets dezincified and the entire surface, inside surface that means the entire inside surface becomes depleted with zinc and enriched with copper this is layer type, and plug type that could happen for example if this is the pipeline and some part is dezincified or dezincification happens in some portion and another portion the rest of the portion doesn't happen, its uniform almost uniform corrosion but that localized section that could get the situation that is dezincification this happens in case of boiler water pipeline and that handling the outside is gas, hot gas and inside is water and that time the block type dezincification happens, that means the localized, so if we have dezincification then the surface becomes enriched with copper.

Now whenever we have let's say A and B, these two elements constitute a particular alloy and if A is noble, and B is active in comparison to these two metals that time if you have enrichment of that alloy with element A, that times we generally see that the corrosion resistance of that particular alloy increases if that, that's alloy is enriched with A, that means let's say I've started with 70:30, if I go to 80:20 this brass will have higher resistance, corrosion resistance compared to this base, so this has high resistance, high corrosion resistance compared to this. So now during dezincification the surface becomes, this is the surface initially the surface 70:30, let's say 70:30 copper by brass, now after dezincification the surface become enriched with copper and there the copper content goes up to 80% let's say, now that time the surface mobility increases but the point is the copper what is enriched here that is not a solid copper, it's basically a porous mass, and that decreases its mechanical strength, so though the corrosion resistance improves but actually the, because of this dezincification the brass is losing its strength, so this is another characteristics so that's why if you want to see whether dezincification has already started or not, the best way to do is basically seeing the mechanical property or the tensile behavior of that material.

Now before the dezincification the tensile behavior is something but after dezincification you will see that the strength decreases, so that is one indication that dezincification is happening even if you don't see this color change still you can see that there is a lot of decrease in strength, so this is another characteristic of dezincification. Now and of course if you see that if you have a less zinc in a particular brass that brass would have higher strength towards dezincification compared to the brass which has higher zinc content. Now let's say if the zinc content is such that beta phase forms in case of brass phase diagram if you go you will see that that the beta phase forms at higher brass zinc content, and if you have a mixture let's say you have a mixture where you have alpha phase and you have beta phase then the dezincification starts in the beta phase and of course this beta and alpha that also constitutes a galvanic cell and it starts from here and then it extends to this alpha phase, this is one observation that is made, that is generally common in case of brass with higher zinc content and if it has beta phase in the Alpha matrix.

Now fourth characteristic is whenever you have conducive condition, let's say you have crevice formation, let’s say pipeline, a pipeline and in that pipeline you have some dirt particle, okay, so then you have crevice formation, you have crevice formation, like this dirt formation there is a crevice, there is a crevice, so that crevice, whenever crevice forms initially that corrosion starts with crevice and once crevice happens then the dezincification goes on, so whenever you have some foreign deposits that would help dezincification, so that is not good in order to, and that is not good with respect to this dezincification phenomena. Now as I have mentioned the metal structure, this is the structure effect metal composition those are very important issue for, in case of dezincification.

Now let us get into the mechanism part why the noble metal stays back and active metal goes out in the form of ions. If you check the mechanism there are actually three school of thoughts, one school of thought says that if you have copper and zinc, zinc preferentially goes out and forms Zn^{++} ions and copper stays back, so in a system like this zinc gradually, zinc is going out in the form of ions, form of ions and gradually the system is getting dezincification. Now in this theory the main problem is if we want to, if that we see that the dezincification gradually goes grows in the depth direction, but that time the small, small pores that forms through that pore you have to have solution supply and that would be little difficult so that the rate at which dezincification happens and the rate at which zinc dissolution should occur that always doesn't match so that time you have some confusion regarding this.

Now second mechanism which is almost well accepted theory, it says that copper, zinc, zinc and copper both goes, both go out and then forms copper iron and zinc ion, so both dissolve that means the brass dissolve, so if you have a brass surface let's say this entire section dissolves, now once in a solution you have zinc ion and copper ion since copper has higher reduction potential so copper E0 of copper is greater than E0 of zinc as well as if you want to see the reduction potential of copper ion to copper, and zinc ion to zinc if you compare that then this will be the situation that means even if you don't consider the standard reduction potential in the solution the reduction potential and the reduction potential of copper would be always greater than reduction potential of zinc, now that time since it has a higher reduction potential copper will redeposit back, so actually in this case the reaction is Cu - 2e it goes to Cu++, now in this case it would be Cu++ +2e goes to copper, so copper redeposit back, now when it redeposit back that time you have, the situation would be like this, this section goes out and now you have copper enriched zones, copper enriched zones, and gradually the, this once we have copper enriched zone that becomes noble site or cathodic site, so cathodic reaction would happen preferentially on this sites and rest of the systems you have the same mechanism, so actually zinc goes out, copper goes out in the form of ions and then copper re-deposits back because of the higher reduction ability of copper ion to copper, so this is the second mechanism. Or the third one people say that both the thing will operate simultaneously, so these happens at the same time this can also happen, this is the third school of thoughts, so there we have mainly two mechanism and third one says that there could be combination of this two, so that means this is the mechanism of dezincification.

Now same will operate in case of denickelification that means when in case of copper nickel alloy, if nickel goes out that time it is called denickelification that time it also would be the same mechanism both go out in the form of ion in the solution and then copper re-deposit back, so these are the mechanism. So now the point is if we would like to stop this dezincification what we can do? So one way is now if you come to the prevention mechanism, prevention so generally we would like to go for an alloy or brass where we have less of zinc that time the inherent strength towards dezincification would be better.

Now second case that means a better alloy, bitter alloy means we have a less susceptible alloy that means we have less of zinc. Second case is as we have seen while talking about the different ways to protect, for protection of metals or alloys against corrosion we have seen that somehow if we can take care of the solution aggressiveness that means let's say I remove oxygen content, I remove salt content so that way also we can have a protection against this dezincification, so you can have by aggressiveness of the solution if you can decrease it.

Now third case if we can have a system where we add tin, in case of brass, 70:30 brass if we can add tin that time that means a tin let's say one person then the brass is called admiralty brass, admiralty metal and this tin somehow protects, tin protects the brass the material from dezincification, how it does, what happens, this tin it basically, this makes the system inherently protective against dezincification.

Fourth one is you can add phosphorus arsenic is B that means antimony these are acting as an inhibitor those can act as inhibitor on inhibiting elements, inhibiting elements what they do? They redeposit on the surface of the metal see dezincification is starting but when we are seeing that this step is occurring, this step is occurring that means the re-deposition of copper but instead of that if these elements deposit back and form a thin surface layer so actually you are cutting this particular step so dezincification could be reduced to a great extent.

Now these are basically the overall picture of dezincification, now there are many more examples, let us explain one particular phenomena that is called graphitization. So graphitization is a particular phenomena that occurs in case of cast iron, and the cast iron when the cast iron is grey cast iron, so that time graphitization happen. Now this graphitization generally in metallurgy the graphitization means the breaking down of pearlite into carbide into carbon and ferrite, so if we see the graphitization, graphitization of grey cast iron, grey cast iron, so that case as we are, as I have said that graphitization in case of metallurgy it means that pearlite breaks into ferrite plus carbon, this is called graphitization but in case of corrosion this is a different phenomena, this graphitization this is from metallurgical aspects, but in case of corrosion this means dealloying. In case of corrosion this means dealloying, what happens? If you see the particular structure of grey cast iron there we have ferrite matrix, then we have graphite flakes, these are graphite flakes, these are graphite flakes, now that case graphite access cathode, and iron access anode so you have a galvanic couple between graphite and iron so if you expose this thing into a solution which is mildly corrosive that time this iron goes out in the form of ions and leaving behind graphite, so there is a selective dissolution of iron and the graphite flakes stays back.

Now this graphite flakes are basically, are like this so if this section goes out that means the iron goes out but the graphite flakes would form a network and try to get attached to the surface so there would be a slight change in the surface appearance, but there would not be much of change in a surface dimension so the main dimension will leave, will remain same almost remains same but the graph, and because the graphite flakes are forming in network and that network actually holding the residue, okay, so these residue which is the corrosive, corrosion product so actually the dimension doesn't change, but what is happening? These residue would be a lose mass okay and that lose mass actually is giving detrimental effect to the mechanical property of that grey cast iron, so this is the bad part of graphitization of grey cast iron in corrosion fundamentals where it is basically happening because of dealloying. Now this thing doesn't happen if the corrosive nature of the solution is very aggressive so that time the corrosion is so fast this entire, this actually the network doesn't form it becomes, it goes out so actually that time you have almost uniform corrosion and so you always remain that, that surface would become always having the base metal surface and this part would go off in case of highly corrosive system, highly corrosive solution.

Now this happens with case of graphite grey cast iron because graphite flakes forms but it cannot happen in case of nodular cast iron, so this is the nodules, let's say these are the nodules of graphite, these are the nodules of graphite, now when we have this dezincification these nodules are basically no longer would be able to form a network, so the entire residue will fall off, so that time the surface would not have the nature what would be possible in case of graphitization of grey cast iron because of the network formation of due to the graphite flakes and in this case since the nodules cannot hold the residue so this will follow up and the system will decrease its dimension but the actual surface would always let say this much graphite, dissolution have taken place so these surface would have the same strength level of the base metal, so this is not a problem for nodular cast iron, so this is about the graphitization of grey cast iron, this is an example of dealloying phenomena also, and dealloying phenomena by applying this dealloying phenomena we can also develop nano porous template of silver or gold, nano porous gold or silver substrate we can develop by this dealloying phenomena, so this is basically helpful, this actual process though it is not good for brass material, but this is good for something else and because of this dealloying gold or silver nano porous gold or silver that can be made. For example, if you have Ag + Zn alloy and that alloy if you allow it to dissolve zinc preferentially then if you have a thin film of these alloy then the zinc goes out and the system would become like this, so it was basically made of silver then and the silver network would form and the silver network will create of porous material and porous template and those 4 dimension will be in the range of nanometer dimension, so the nano porous gold or silver template can be made by using this particular phenomena called dealloying, so it's a corrosion phenomena is not always bad, it is good in this case by applying the simple principle we can have a very good nano porous gold or silver template, so this is about dezincification, dealloying, graphitization of grey cast iron.

So now let us get into another form of corrosion so that is basically the erosion corrosion. So this is another form of corrosion, this is erosion corrosion and now erosion corrosion is due to the relative movement of solution over the metal or alloy surface, so now if this metal surface, this is the metal or alloy surface over that the solution is, this is metal surface and the solution is moving and that means there is a relative movement between the solution and the substrate or the metal. Now due to this movement of solution if there is acceleration of corrosion, if there is acceleration of corrosion rate or acceleration of corrosion, acceleration of corrosion that time the phenomena that process is basically due to erosion effect of the solution. Now if there is reduction of corrosion rate or deceleration of corrosion then that will not be termed as erosion corrosion because of the flow of the solution, now before that before coming to the deceleration effect we always should understand that these erosion corrosion would generally increase the corrosion rate because of the relative movement of the solution over the metal surface and let's say when the corrosion is happening that time there will always be a sort of directional nature of the corrosion attack. Now the gradually the surface layer would go off and then you will have since the solution is flowing like this so the nature of attack would be like this, that means we have a directional nature of corrosion attack on the metal surface and gradually there would be acceleration of corrosion.

Now if this solution movement is very high, let’s say the solution movement is very high that time apart from this dissolution effect there could be wear effect, there could be wear effect, because of the movement of the solution and if the solution contains lot of dust particle or the slow in the form of slurry that would also give the wear effect on the surface if the movement solution velocity is very high, so wear effect as well as the corrosion and then even if the wear effect is not there only because of this movement there would be acceleration of corrosion. Now let's say in case of pitting we have said, we have seen that pitting initially forms like this there will be several pits like this and in case and that for pitting one necessary condition is stagnancy of the solution, stagnancy of the solution. Now if, and we have seen that even the experimental evidence source that if the solution velocity increases, the pitting rate also decreases, so solution increases, pitting decreases, now that means because of increase in solution velocity one particular type of corrosion phenomena which is very insidious or very dangerous with respect the material property under reuse that time because of the solution velocity pitting resistance improves or the pitting decreases that could not be termed as erosion corrosion because here there is a deceleration, there is a decrease in corrosion rate, there is a decrease in corrosion rate, this will not be a phenomena, this will not be under erosion corrosion, this is not an example of erosion corrosion so that means we have to always see if there is any acceleration of corrosion.

And now this metal, how this could be possible? Metal will go into solution, metal goes into solution metal -2A goes to solution and the solution dissolution rate increases because of the erosion effect, how? Let's say if we consider a particular material, soft material let's say that is lead, lead or copper the soft material because of those erosion effect there could be localized deformation and that deformation could increase the, could possibly form a local galvanic cell because the deform part and on deform part that could be having galvanic coupling effect and so the un-deformed part would dissolve quickly or if there could be a possibility of a deform part which becomes embrittle and that goes off because of the erosion effect, or the movement effect this is possible in case of and this is basically a dissolution of metal ion.

Now this can also be possible if there is surface layer, now let's say in this case we have a surface layer, this is the metal surface, this is metal and this is passive layer and let's say this is some oxide, now because of this erosion effect, now there could be a localized removal of passive layer. Now once there is a localized removal of the passive layer that means the metal surface is exposed to the solution and then before the passive, another passive layer forms by that time there could be little more dissolution like this.

Now second phenomena would be this part there could be little more chipping away of this passive layer so again the dissolve the metal surface is exposed to the solution or the corrosive, little more corrosion again happens and there would be a formation of passive layer, so before it forms another passive layer till that period the metal surface is exposed to the corrosive and that time the metal dissolution would enhance and once the passive layer forms then metal corrosion would be sluggish, but the point is during that process some other part of the passive layer would get damaged again, so during that process also the metal surface is exposed to the solution, dissolution happens, rapid rate of dissolution happens before it re-passivates. So this is another mechanism by which erosion corrosion can happen. And where it could happen severely? For example, if we have let’s say a pipeline, the pipeline the metal solution is moving and generally until and unless the pipeline has a break or bend, let’s say this is a bend, this is a bend in the pipeline till that moment the solution always achieve a linear flow, laminar flow, and that is not that dangerous, but once the solution is changing its path movement direction that point this place there could be a huge turbulence, and this turbulence effect is very dangerous if you consider erosion corrosion, and due to this turbulence this part of the metal bend would be susceptible to erosion corrosion to a great extent, and there could be a break in this section, wherever turbulence develops, so that means we have, whenever we have change in direction that is a very susceptible part in the structure, so we have the appearance, there could be appearance of whenever we have grooves, grooves whenever we have gullies, whenever we have waves, so that means this is wavy nature, so that means the appearance of the erosion corrosion those are rounded hold, so these are the appearance of erosion corrosion and this can happen whenever we have a direction change or whenever we have a lot of residual, lot of dust particle is there in the solution, so these are the appearance of erosion corrosion.

So we see the appearance that is shown by erosion corrosion effect are basically grooves, gullies, waves, rounded holes, those are the appearances and as well as we have seen that there could be a directional nature of erosion corrosion on the metal surface. Now this erosion effect can also be produced not only the solution even by the gases, now let's say a metal surface, on the metal surface this is my metal surface and if oxygen gas flows that time there could be oxide layer formation, thin oxide layer formation but due to this high velocity gas and if the oxide layer is not that adherent to the surface locally some of the oxide layer could get damaged until it forms another oxide layer, so it will form further oxidation so there would be a dip in the system, so like that the entire section could get damaged and the fresh metal surface is exposed to hot oxygen gas, sorry hot gases it could be $CO2$ mixture, $CO2 + O2$ mixture, so or CO gas so that gas can damage the surface by erosion effect. Now it can also be formed by liquid metal, if a chamber is holding a liquid metal that metal due to the relative movement of the metal the metal surface could get damaged and that is a part of erosion corrosion also. Now as we have said that solid particle which are in the solution, moving solution those solid particle can be detrimental towards the erosion, detrimental and that can lead to erosion corrosion, so solid particle, solid particle can erode the metal surface and there could be erosion effect, and the solid particle if it is a passivating metal that case the solid particle can damage the passive layer and before the passive layer forms very high degree of corrosion can possible, can be possible, and if we have a moving gas, hot gas that could also lead to erosion corrosion.

Now systems which are under erosion corrosion effect, now what are the systems which are under erosion corrosion effect? One is piping system, then we have in case of piping system there are few sections which are much more susceptible to erosion corrosion for example bends, then we have elbows, then we have particular bends and elbows and sharp turning, or let's say one big pipe is coming and there is a, let's say this pipe the large dimension pipe, the fluid is flowing and from that you have a outlet which is small dimension, and this part is more susceptible to erosion corrosion, why? And this also under the effect of turbulence, and what happens? Now this section we have laminar flow and suddenly when it enters into a smaller cross-section area this part there will be turbulence formation, there will be lot of turbulence and before the solution assumes laminar flow so this part is laminar poor flow, so that means after entering into the shorter dimension or shorter cross-section pipe the fluid assumes a limited laminar flow after a short distance but till that point this section there will be lot of turbulence and due to that effect the corrosion would be more in this section, so this is another effect, another system or situation where we can experience erosion corrosion.

Then we have pumps, then we have propellers, then we have impellers, so these are the systems where we can have lot of erosion corrosion effect, even we can have a nozzle duct, nozzle duct then orifice, so those cases even turbine blades there we can experience erosion corrosion effect, so these are the systems or situations where we can experience erosion corrosion effect. And before I come to different factors which will affect erosion corrosion effect let me mention that, let's say we have a very good laboratory data for a particular metal or alloy system which shows very good corrosion resistance, but it may not be true that system will show very good corrosion resistance in moving system or whenever you have a relative movement of the solution or the liquid that it handles then the corrosion rate would be entirely different because in the laboratory we have almost all the tests are done in static condition mostly and even if we have some sort of movement that would be a very, very small movement so it will not actually depict the actual scenario, so the laboratory test data cannot be considered for judging the erosion corrosion resistance of a particular metals and alloys.

Now let us get into different factors that will guide erosion corrosion, one is definitely the surface film, nature of surface film how strong it is, how adherent it is to the metal surface that would decide the erosion corrosion resistance of that particular metals and alloys. Now in case of surface film one more criteria of course the strength, adherence, then you have let's say the surface film is very compact and very less of defect, that surface film would definitely act better in order to have, and it would have very good resistance against erosion corrosion. And there are two other criterias, one criteria is the rate of passivity attainment, this means how quickly the passivity is attained again, let's say a metal surface this is my passive layer, this is my passive layer if some section is broken, some section is broken, now that case if this section is broken that case how quickly the metal surface the broken layer, the metal which is exposed to the solution that will form the passive layer, how quickly it will form? The quickness of attaining passivity would decide the erosion corrosion property of that particular, erosion corrosion resistance of that particular metals and alloys, so the quickness of attainment of passivity and of course its strength to resist wear effect, wear effect and of course the continuity, continuous nature, continuous nature of the passive film those will decide the erosion corrosion resistance of a particular metals and alloy, of a particular metal or an alloy.

Now second effect is, second effect is velocity, now while we consider velocity we must realize that the velocity would be a factor whenever there is enhancement in the corrosion rate that is basically that in the definition we have seen the erosion corrosion says that there should be enhancement in corrosion rate and if there is decrease in corrosion rate that should not be considered as erosion corrosion. Now when we consider velocity, we generally experience a critical velocity for a particular metal when it is exposed to a particular medium a critical velocity before that the corrosion rate would be very sluggish but once the critical velocity is reached then the corrosion rate would enhance quickly, so why that happens? Generally it's related to a breaking down of the passive film or dissolution of passive film that would lead to enhancement in corrosion rate, so the critical velocity is important issue so we can decide for a particular metal or alloy system what could be the critical velocity when it is exposed to a particular corrosive medium.

Now then this velocity that means this is the characteristics of velocity affect, critical velocities to be attained before we experience exaggerated effect of erosion corrosion. Then second issue is it always increases the corrosion rate, why? There are two ways, one is let's say oxygen, dissolve oxygen is there or dissolve CO2 is there in the solution, and if let’s say a particular section oxygen is depleted, particular section oxygen is depleted because of velocity the oxygen depleted oxygen part will be recovered because of movement issue, because of the solution movement and oxygen concentration would be same throughout. And then it increases the diffusion or transfer of ions, let's say I have a particular metal surface where passive layer is forming, now that passive layer always you need, if it is a stagnant solution at that particular temperature until and unless metal dissolution is of course taking place, but at that temperature if it is stagnant then the metal ion concentration once it reaches some critical value because of the solubility effect of that passive layer the metal ion will form a passive film, and the passive film will grow up, but if somehow I drive away all those metal ions that are forming on this metal surface and which are in equilibrium with the metal and the solution with the passive layer in the solution and if we can break the equilibrium, so more and more metal ion should come in order to maintain that solubility. Now once this happens though that time this passive layer thickness goes down, passive layer thickness gradually goes down and then you have more and more metal dissolution, so this is second effect that is basically, because of this we have enhanced corrosion rate due to velocity, increase in velocity, but velocity sometime decreases the corrosion rate, for example if we have inhibitor which is added in the solution, now that inhibitor can go to the section where the enhanced attack is forming, enhanced attack is going on so that inhibitor, because of this flow of the solution inhibitor can go there and stop the corrosion effect, so this is the effect of inhibitor, so inhibitor can reduce the corrosion rate and that is happening because of the velocity and that moving liquid will transport that inhibitor to the section where we have more corrosion and that inhibitor will try to control the corrosion rate. Now this is basically the velocity effect, now there are some case studies and these case studies involve the surface film as well as velocity.

Now for example if we consider lead pipe, and if we consider lead, now that lead pipe can handle H_2SO_4, dilute H_2SO_4 for a long duration and that time we have lead oxide or lead sulfate, those films form on the lead surface when it is exposed to dilute H_2SO_4 and it gives very good protection, it gives very good protection because of this passive layer formation and it can be operational for twenty years.

Now if the solution strength increased and it goes to low to high strength, this is case studies, case study one and if it goes to low to high strength lead sulfate dissolves and once lead sulfate dissolves now you have lesser productivity of that passive film over the lead surface, so lead dissolution increases to a great extent, so that means it's not only velocity at the same time strength of the solution would decide whether the passive film would be active or not, active means whether it would be active to give protection against this erosion corrosion.

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