Corrosion - Part I
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Lecture - 06
Forms of corrosion: Explanation with examples

Hello everyone. Let us start our 6th lecture, and till 5th lecture, we completed pitting Corrosion Mode. And we have seen that compared to uniform corrosion galvanic crevice as well as pitting mode of Forms of Corrosion, they are not; I would say they are a deadly forms of corrosion compared to galvanic, I would say pitting as well as crevice they are not at all desirable, because they degrade the durability of a component made out of a methyl or alloy. Now, we will continue our discussion on rest four forms.

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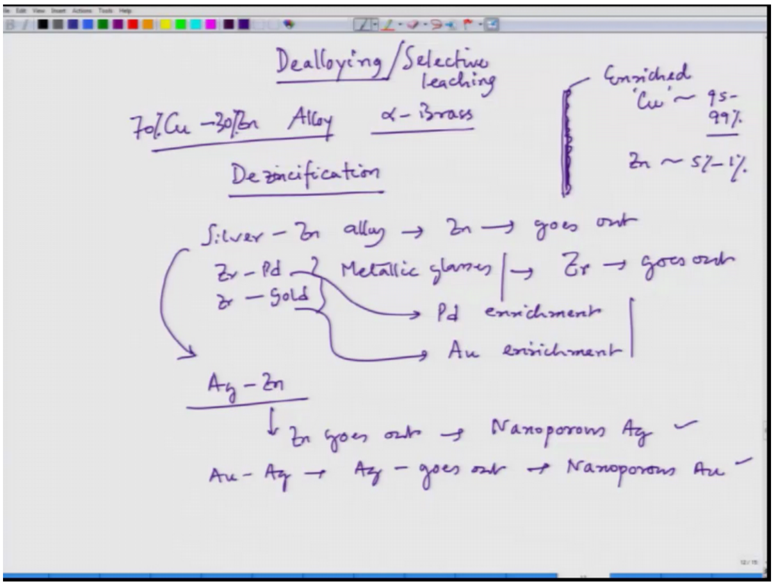

Dealloying/Selective leaching

70% Cu – 30% Zn Alloy α – Brass

Dezincification

Enriched 'Cu' ~ 95-99%

Zn ~ 5% – 1%

Silver – Zn alloy → Zn → goes out

Zr – Pd } Metallic glasses → Zr → goes out

Zr – Gold

→ Pd enrichment

→ Au enrichment

Ag – Zn

↓ Zn goes out → Nanoporous Ag

Au – Ag → Ag – goes out → Nanoporous Au

So, we are left with four other forms one is dealloying. Dealloying a kind of corrosion form, where one of the elements in an alloy preferentially dissolves. For example, if we consider copper zinc alloy, if we consider 70 percent copper and 30 percent zinc which is called alpha brass, there we do experience dealloying where zinc which is very active component when copper and zinc are together.

So, zinc dissolves in the solution or in electrolyte copper stage back. So, if we have a surface like this copper zinc surface, on this surface we have enriched copper. So, the concentration of copper can go even up to 95 to 99 percent. Initially it was 70 percent, now it has gone go 99 to 99 percent and of course, the zinc content would be 5 percent to 1 percent and it was 30 percent now it has reduced to 5 to 1 percent.

So, here we call it dezincification, it has got another name which is called selective leaching. So, this dealloying can be observed in many other situations, like silver zinc, like zirconium palladium alloy, like zirconium gold alloy. So, all those cases we do see dealloying and in all cases for example, here zinc goes out and silver is left out. So, silver enriched region is formed. These two are typically example of metallic glasses.

If we do little bit of if we do rapid solidification, they lose their crystal in structure and they form, random arrangement of atoms just like what we see in liquid phase, but that is in solid condition and that time we call it metallic glass. And if we leave this particular two alloys in axial solution, then zirconium, this is zirconium goes out. And in this case we have Pd enrichment and in this case gold enrichment.

So, here also this is dealloying since zirconium is going out, this dealloying is not good for some situations like brass. If we have a water pipeline designed for carrying portable water, drinking water; the inner wall of the pipeline, they can experience dezincification, the copper enrichment happens and these copper region is loosely stuck to the inner surface.

Now, these copper region also is also porous. So, after sometime it might crack, it might break, the pipe might break or pipe might leak. So, from the point of holding the structure, this is not good. But interestingly has we have talked in the first lecture that this dealloying can be used in the positive sense, like nowadays we are trying to make porous structures and of course, nanoporous structures. The porosity size of the porosity is in the nano metric range.

And when we have this, this porous structure can be used as a very good catalysts, or it can be used for active surfaces for many other purposes like medicines and drug deliveries and all those cases. For example, if we consider silver zinc, then zinc goes out and it leads Nanoporous silver.

For example, Au silver Ag goes out in the solution and it leads Nanoporous Au. So, these things can be used as very good catalysts. So, this is the positive sense we can make use of dealloying or selective leaching; this is another forms of corrosion.

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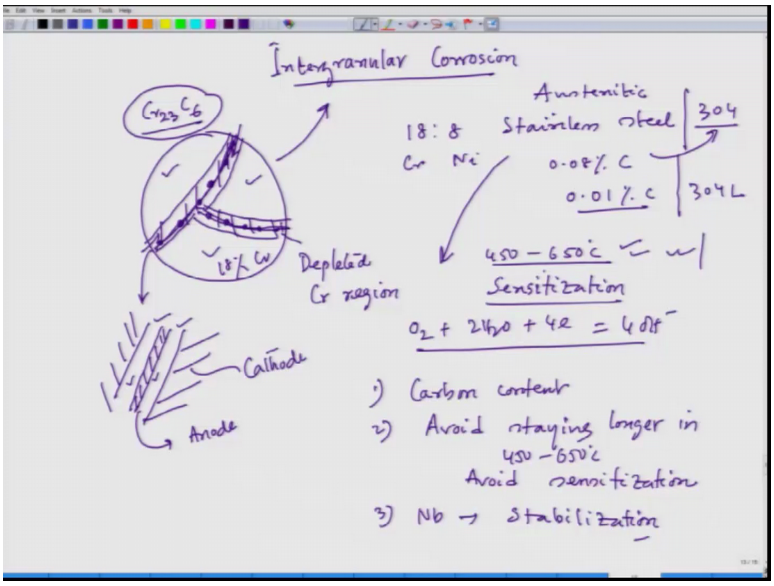
Intergranular Corrosion

$O_2 + 2H_2O + 4e = 4OH^-$

1) Carbon content
2) Avoid staying longer in 450 – 650°C
Avoid sensitization
3) Nb → Stabilization

Now, if we come to intergranular corrosion where from this name, it is very clear that corrosion would take place along the grains. For example, if we have a structure like this, where you have grain boundaries; the corrosion would go along the grain boundaries, that is what this name intergranular corrosion. Classic example is 18 8 stainless steel. An 18 percent which is weight percent is chromium and 8 percent nickel, when we have 8 percent nickel that time the structure becomes austenitic; austenitic stainless steel. And this austenitic stainless steel can be made at a very low carbon content or moderately high carbon content for example, normal stainless steel contains 0.08 percent carbon. And this is the typical 304 tritium of this particular steel.

Now, if it is this is 304; if it is 304 L that means, carbon content goes to 0.01 percent. Now in this case, if we consider 304 which is containing 0.8 percent carbon. There if we hold this particular steel in the temperature region around 450 to 650 degree Celsius hold for a longer duration, then one peculiar thing happens.

Now, in case of stainless steel the stainless property is derived from this chromium content. The chromium actually reacts with atmospheric oxygen and, then forms chromium oxide which is a thin layer on top of this stainless steel which gives the stainless property. So, oxidation is not always bad. So, actually this because of the chromium oxide it gives the stainless property to the stainless steel.

Now, when we hold this steel around this temperature region and if we have this grain structures grain boundary structures, the chromium carbide nucleates along the grain boundaries. These are chromium carbide and this is chromium 23 C 6, this carbide nucleates on this grain boundaries; in case if this steel. And when it nucleates occurs, there would be surrounding regions the surrounding portions will be depleted with chromium. So, this is depleted chromium region.

Since stainless property is derived from chromium oxide and interestingly here, also just like zinc and zinc oxide, chromium oxide is also cathodic in nature compared to iron. Now, in this region we have eighteen percent chromium. So, there we have a chromium oxide layer. Now along the grain boundaries, we have higher chromium content, because the chromium carbides are precipitated over there, because the grain boundary is active plus for the precipitation.

Now, there also we have chromium oxide. So, now, the typical situation is we have two situations the centre region we have chromium oxide and then around this a region we have chromium oxide, but in this region we do not have chromium oxide. And since the chromium oxide is cathodic in nature; so, cathodic in nature is as compared to the iron surface with the depleted chromium. So, cathodic reaction would happen on the chromium oxide, wherever we have chromium oxide.

So, we have a huge area where cathodic reactions are taken place. And of course, if it is dipped in NaCl solution which is neutral the cathodic reaction of course, here would be O 2 plus 2 H 2 O plus 4 e equal to 4 OH minus. So, these cathodic reactions happens on the huge chromium oxide covered regions, and the small region this is this region which would act as anode. So, these are acting as anode and this region acting as cathode.

And since the anodic region is narrow, so, small area and the huge cathodic area so, the anodic region would corroded at a very very fast rate compared to the very very fast rate in this particular situations. So, galvanic effect is felt at the same time the area factor is also governing this corrosion, very high rate of corrosion along the grain boundary. And then what would be experienced? The attack would be along the grain boundary and that is what it become intergranular corrosion.

This kind of corrosion attack is also possible in some aluminum alloys, in some nickel base alloys, where we have also carbon, there was be also possibility of formation of chromium carbide along the grain boundaries. So, there also we can have a these kind of intergranular corrosion.

Now, just to continue on this how to stop them, the stopping character is this particular chromium oxide is the culprit. So, somehow we have to stop this chromium carbide formation along the grain boundary. How can we stop chromium carbide formation? One route is of course, if we reduce carbon content. So, if we do not have carbon for the precipitation of chromium carbide of course, chromium carbide would not precipitate. So, the chromium would be distributed homogenously over the entire surface. So, there will be no formation of a preferential anode and a large area cathode. So, we can avoid intergranular corrosion.

Second part is of course, this temperature region. See, if we can avoid staying longer in 450 to 650 degree Celsius. And when you hold this steel in this temperature region and when this chromium carbide forms along the grain boundary, we call this particular phenomena sensitization. So, avoid now let us say we do not want to get rid off carbon. Steel we would like to prevent sensitization, how can I do it? If we add niobium into it, see the niobium has got a higher affinity towards carbon. So, it forms niobium carbide. So, that the formation of chromium carbide is avoided because there is no more carbon available for chromium carbide formation.

So, again this stabilize sensitization can be avoided and when we add this niobium kind of higher affinity elements to the stainless steel, we call it stabilization. So, let us not go ahead with this intergranular corrosion any more.

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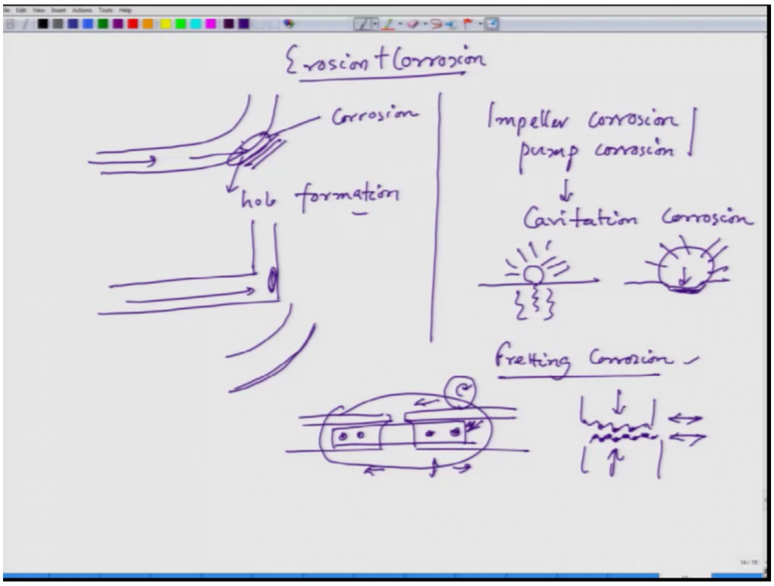

So, let us go to the another form of corrosion which is erosion corrosion. In case of erosion corrosion, as the name suggest that there would be a flow which we will involve wire of this material and plus corrosion so; that means, erosion plus corrosion. So, like a kind of pipeline, where we are flowing water and that water if it contains suspended particles.

Then when it is moves, it will hit this particular region. So, when it hits,,what it will try? It will try to deform that regions locally, or it will try to remove material by wire mechanism. So, when we have that kind of situation, the corrosion rate around this region would be also high. So, then gradually if we keep having this particular flow at some point of time these region, there could be a hole formation. This is a typical example of erosion corrosion.

Now here also the designed part would definitely come into picture. Now, if we have a design like this the pipeline design, the erosion corrosion tendency would be much fast, much higher. It will be felt more, because the effect of turbulence here. Now, if we have a flat section, we make gradual change in slope, or the corner then erosion effect would be less because the turbulence is avoided it is a typical design aspects.

Now of course, the material is one aspect. We have to have a better material which will have a inherent erosion corrosion resistance, just like instead of politic steel, we can go for temper martensite and nowadays people are thinking of benthic steel which would have a much higher erosion corrosion resistance. These are all in the research regime. Now, if we consider two definite two forms of erosion corrosion, which are typically experienced like impeller corrosion or pump corrosion.

Now, many times if we go and look at the blades of the pump water pump, we see that the edges of the blades are heavily corroded and many a times we see that the edges of the blades are basically detached from the original shape original structure. These happens because of a typical corrosion which is called cavitations. In case of cavitation what happens? Because of the pressure change water bubbles forms and then when the pressure increases, this water bubbles collapse on the metal surface.

So, this formation of bubble and collapse of the bubble during bubble for collapse, the kind of shock waves it generates that shock waves goes towards, this towards the metal side. And this shock waves can even deform the base deform the metal surface. So, once we have deformation; that means, it is becoming active. So, once it becomes active; that means, the corrosion rate is also increasing compared to the region where the bubbles are not forming and then prolong corrosion of that region.

So, now, because of this bubble for collapse there is a small dent and once you have a small dent, that we will nucleate another bubble around that region. So, another collapse and then shockwave generation this will be deformed further and it will be corroded further. So, like that way this goes on this is the kind of cavitation corrosion which is bubble formation and, then collapse of the bubble because of the pressure change. So, these also has got a scientific explanation to it, but we are not looking at that. So, I have just giving some kind of eye views that this is a form of corrosion

And another corrosion special type of erosion corrosion is fretting corrosion. In case of fretting corrosion, we do experience this fretting corrosion near the fish plate, you might have seen fish plate. This is basically the two adjoining rails they have joined by fish plate. So, you have a rail two rails are coming. So, this is a rail, another rail is like this; this is a rail two rails. So, you have holes here. you have holes here; so, we and then you have a plate which connects this two rails tightly and these is called fish plate and these fish plate are tightened regular bases.

Now, when a rail moves on the surface, there would be a small vibration around that fish plate region, the vibration could be this way or it could be this way, because of expansion and contraction. And these particular vibration is so small, this amplitude is so small that it remains in the fretting region and, when this fretting happens this vibration happens. Since they are tightened, there could be a formation of oxides in that interface between fretting this fish plate of the steel of this particular rail.

And because of this fretting action for example, oxide forms this two surfaces. And there is a small amplitude vibration and it is under load because the train is come falling on it. So, then these regions might get dislodged. So, a kind of erosion is taking place or wire is taking place. And now once the train goes out they might get oxidized, because also the temperature goes up.

So, now, you can have oxidation first and then erosion, or you can have erosion first and then oxidation and finally, you would see that in this particular small dips there could be possibility of debris accumulation. So, this debris will act further during the next fretting action when the train moves. So, this is the typical fretting corrosion. And interestingly you might see that time to time some a railway person comes and tightened this fish plates, because this fish plate loosens and this loosens, because of this fretting action ok.

And this here also we have a we have a kind of fear of crevice corrosion, because these are also acting as a crevice connection; if waterfalls water stays, there it remains stagnant the corrosion takes place.

So, in order to avoid this fretting corrosion why people do put grease kind of object a lubricant, which will reduce this friction effect. And also this lubrication helps in avoiding crevice effect, because it will not allow the water increase in to this crevice. So, two ways it acts. So, like that there are cavitation, fretting, erosion, corrosion; there are many examples. So, we are not looking at this, but this is kind of bird's eye view that what is erosion corrosion.

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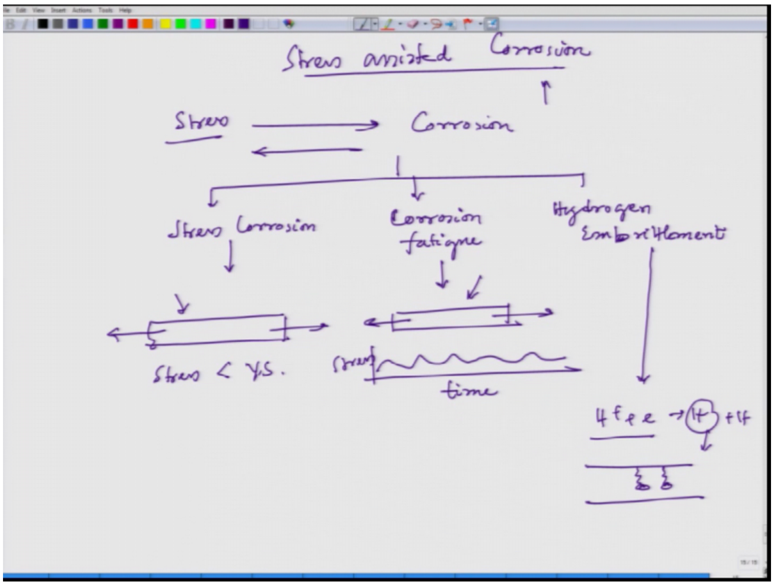

And finally we have stress assisted corrosion. In case of stress assisted corrosion as the name suggest again. So, we have corrosion and then stress is also helping or it can be other way around, stress should be there corrosion would also aggravate the attack. Now, stress associate corrosion. They can be divide into three parts: one is Stress Corrosion, another one is Corrosion Fatigue and then, high we have Hydrogen Embrittlement.

In case of stress corrosion, if an object is component is under tensile stress and if it is exposed to the corrosive, then if the stress is less than yield stress of the component and if we combine corrosion, an interesting in this case this particular loading is stagnant. So, we are not having alternate loading just like fatigue. So, that case the kind of stress corrosion we experience we call it stress corrosion. We call it stress corrosion because it is a stagnant form of corrosion along with the stress.

But incase for corrosion fatigue, we have a component and that time we have alternate stress alternate stress. So, it can go towards tensile component as well as compressive component and that time you have a corrosive effect that particular failure would be considered as corrosion fatigue. Just like what we have to experienced in case of silver breach as we have given example in the first lecture. So, people think that the corrosion stress corrosion, as well as corrosion fatigue they are the two culprits for having catastrophe in that breach failure.

And the another effect which is called hydrogen embrittlement. In many situations, if they are acting if the component is in active hydrogen environment. Active hydrogen means for example, there is some cathodic reaction plus e this reaction is taking place. So, this hydrogen before it combines with another hydrogen, these hydrogen atomic hydrogen is very very active and these hydrogen can react with hydrate forming elements in present in steel like hydrate forming element like titanium, which will allow a formation of brittle intermetallics in front of a crack tip and they will go for a brittle mode of fracture.

So, this is hydrogen embrittlement there could be a possibility of hydrogen blister also. These hydrogen elements; for example, in this hydrogen is going in inside the metal by diffusion. And then around inside region hydrogen can combine each other from hydrogen gas and they will form blister. So, those kind of diffuse can be possible. So, these happens because when we have an existence of atomic hydrogen formation due to some cathodic reaction; this cathodic reaction.

So, these particular forms stress corrosion corrosion fatigue and hydrogen embrittlement, they generally lead to catastrophic, or a kind of sudden failure of the component. And those failures could be along the grain boundary for example, in case of a sensitized stainless steel. If we have stress effect also, they will the corrosion and stress, they will allow this particular material to fell along the grain boundaries. So, you will have a inter granular corrosion and intergranular kind of stress corrosion in that case.

It can be also transgranular nature. So, there are many theories for stress corrosion fatigue and hydrogen embrittlement. So, we would not look at all those theories, but in a nut shell, this is a kind of stress corrosion fatigue and hydrogen embrittlement. And these leads to many a times catastrophe and this main thing is they will not give you any signature that it is failing; it fails suddenly ok.

So, now, we have looked at different forms of corrosion. So, now, we would step into our fundamentals aspects which are basically electro chemical nature of corrosion and its thermodynamics and kinetics and finally, we will relate the thermodynamics and kinetics to understand the corrosion phenomena in metals, or alloys let us stop here.

Thank you