Corrosion Failures and Analysis

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Lecture - 19
Intergranular corrosion

Welcome back to the course Corrosion Failures and Analysis. Today, we have lecture 19 and today, we will start another form of corrosion which is called Intergranular corrosion. As the name suggest you see that it happens along the grain boundary.

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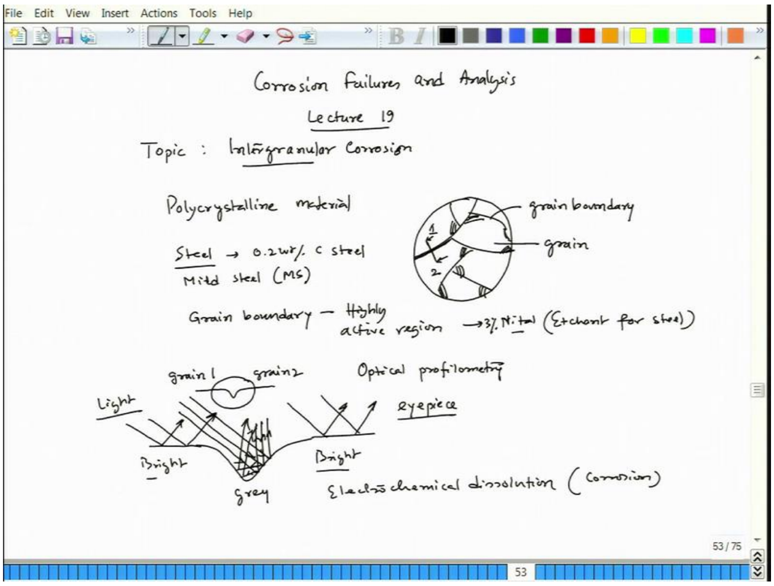

Now, in case of steel let us say; let us say 0.2 weight percent carbon steel or carbon manganese steel little bit of silicon in it. We call it mild steel or MS, ok. So, in that steel if you see the micro structure after doing proper metallographic polishing and etching in nital we get to see that under optical microscope the micro structure would look like this with little bit of pearlite along the grain corners, ok.

So, this kind of micro structure you would see, but at the same time you would see a clear distinction between two grains with a line thin line. And since in optical microscope it is basically we are seeing the image because of the light reflecting out of the surface and it is coming through the eye piece to the eye and that is what you are seeing the micro structure, ok.

And, in the micro structure you are seeing that this portion the grain boundary portion is black ok or dark compared to the other region. Other region would be shining or greyish color little little light grey greyish color, but the grain boundary would be clearly a dark portion dark thin line.

Now, question is why that grain boundary is becoming thin dark line? The reason being because the grain boundary is highly active region highly active region and that is what when you dip it in nital solution which is the typical etchant for steel, ok. So, that time generally 3 percent or 5 percent 3 percent or 5 percent nital we use, sometimes we use 2 percent depending on the activity of the steel.

Now, in case of mild steel we can use 3 percent even 5 percent nital solution, but that time you have to be careful while etching the time of if you do there are two types of etching – one is immersion, another which is another is swab etching. Swab what you do? You take a cotton block, you soak it with nital and then after you prepare scratch free mirror like structure of the steel on top of that you swab or actually you rub that particular cotton ball soaked with nital and then you see the change in color.

You will see that the color changes to grey and once you see that the grey color is overall uniform and then you immediately put it under running water and then wash it with alcohol and then dry it and see it under a microscope. And, when you see it under microscope it looks like this kind of micro structure. I will have a micro structure. I will see in a ppt.

Now, what happens? If you see a cross-section along this cross-section, ok. The cross-section would see that it will be like this if you see the cross-section. So, I am saying that from here I am started looking at the cross section side and here I have I am ending. So, this is one grain, grain 1, this is grain 2.

So, here it is let us say 1, this is 2 and there is a dip and that dip happens because the boundary between two grains reacts heavily in presence of nital and that is what there is a lot of material loss due to electro chemical dissolution and that is what you are going to see a dip here if you see a cross section. Let us say you do optical profilometry what it does? It actually checks the surface roughness and wherever you find a small dip, it should show you that there is a dip.

Now, if you see let us this portion let us make it let us zoom it. So, when you zoom it will look like this. Now, you are sending since it is an optical microscope you are sending light beam. So, these are the light beam which are falling and now, it will try to reflect out ok. So, it will try to reflect out like this. So, it might get reflected like this, it can reflect out like this.

Similarly, it can reflect like this, it can reflect out like this. So, like that there will be a multiple reflection of a light beam within that dip region, ok or we can say valley, but if you see the same parallel beam is coming. So, from there light will reflect and go to eye piece, fine. Now, this is the light ray or you can say white light. So, this light ray is coming to eye piece, but here this light is also trying to come to the eye piece.

But since they are having multiple reflection there will be lot of absorption of light and since that is what the light beam what would come to eye would be much lesser intensity than the light beam which is coming from flat portion of the particular grains, ok. So, that is what this portion would look grey and this portion would look bright this portion would also look bright.

So, that means, that is why the grain boundary looks dark in nature because there are lot of multiple reflection and lot of loss of energies of the light beam because of the multiple reflection and absorption and that is what you are not getting sufficient light coming from that particular valley region. So, that is what it becomes dark colour.

Now, question is here also the grain boundary is attacked preferentially compared to the outer other regions. So, now, intergranular means the preferential attack along the grain boundary ok preferential corrosion of along the grain boundary. Here also this is and since it is a nital solution this is also electro chemical dissolution and electro chemical dissolution is nothing but corrosion. So, that means, grain boundary is preferentially getting corroded.

So, you should say that this should be inter granular corrosion, but coming to the point that intergranular corrosion, when we see the surface pattern it does not this particular dissolution does not go very deep inside the grain boundary. If you see this depth part it does not go very deep ok.

It stays on the surface only because the activity of the grain boundary is not that high compared to the cases where we get to see intergranular corrosion and there the attack or the corrosion attack along the grain boundary is deep inside the material. It does not happen on a shallow depth, it happens at a much deeper section of that along the grain boundary.

So, this also can be convert can be termed as a grain boundary, but to a specific sense we term grain boundary when there is a specific attack along the grain boundary and that attack goes deep inside the body ok. And that attack happens because of another aspect of that grain boundary attack is when we have intergranular corrosion, that particular time there should be a formation of precipitates along the grain boundary, ok or there could be possibility of precipitate free zones along the grain boundary, ok.

So, those two cases should happen in parallel with the specific attack along the grain boundary. So, in case of mild steel this should have been a grain boundary attack because it is only grain boundary is getting attacked, but this may not be coming under the gamut of intergranular corrosion; because in order to have intergranular corrosion there are two more conditions are to be made.

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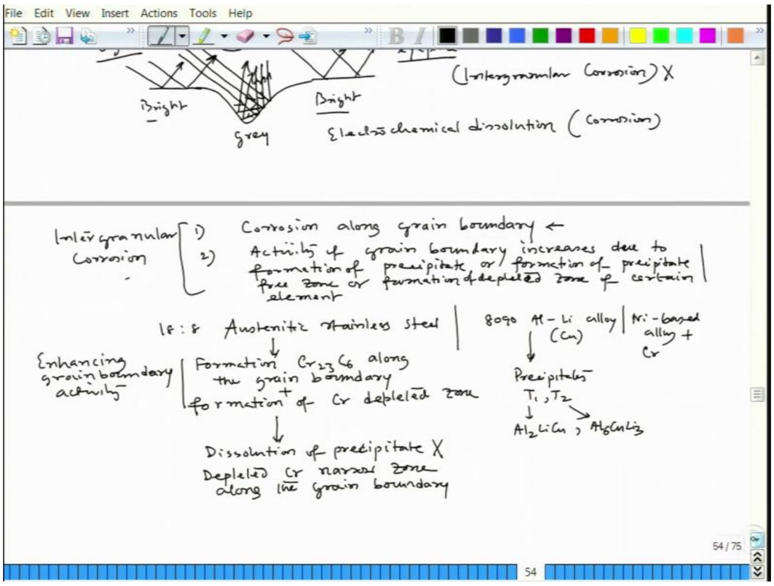

(Intergranular Corrosion) X

Electrochemical dissolution (Corrosion)

Intergranular Corrosion
1) Corrosion along grain boundary ←
2) Activity of grain boundary increases due to formation of precipitate or formation of precipitate free zone or formation of depleted zone of certain element

18 : 8 Austenitic stainless steel | 8090 Al – Li alloy (Cu) | Ni-based alloy + Cr

Enhancing grain boundary activity | Formation $Cr_{23}C_6$ along the grain boundary + formation of Cr depleted zone

↓

Dissolution of precipitate X

Depleted Cr narrow zone along the grain boundary

Precipitates T_1, T_2

Al_2LiCu, Al_6CuLi_3

One is of course, corrosion along grain boundary ok, second is this activity of grain boundary increases due to formation of precipitate or formation of precipitate free zone or formation of depleted zone of certain element, fine. So, then only we can call it intergranular attack fine otherwise we do not term them as intergranular corrosion.

For example, in case of mild steel this grain boundary is also specifically attacked, but this cannot come under the gamut of intergranular attack because we do not have this kind of situation due to the formation of grain boundary precipitate or precipitate free zone or formation of depleted zone of certain elements along the grain boundary, ok. So, that second condition does not meet.

So, that is what this cannot be considered as intergranular corrosion. It cannot be considered as intergranular corrosion. The normal intergranular the grain boundary attack ok, but this one should be consider as intergranular corrosion because of course, corrosion happens along the grain boundary, but at the same time that corrosion happens the reason for that corrosion is enhanced due to the formation of precipitate or formation of precipitate free zone or formation of depleted zone of certain elements.

Now, this precipitates could be cathodic; precipitate could be anodic and the precipitate free zone could be anodic. So, that way are as well as the formation of depleted zone I think I miss this off formation of depleted zone of certain element, ok. So, then only we have enhanced activity along the grain boundary regions and we get intergranular corrosion attack.

Now, this thing happens this particular intergranular corrosion happens when we consider let us say 18: 8 austenitic stainless steel or we can also have it in case of 8090 aluminium lithium alloy or we can have in certain nickel based alloy where we have chromium also plus chromium there we have such kind of situation where grain boundary activity increases.

In this case it increases due to formation of $Cr_{23}C_6$ precipitate along the grain boundary plus formation of chromium depleted zone. So, this happens in this case. So, this is actually enhancing grain boundary activity. Now, in this case we have precipitates of T1 or T2 which are copper base precipitate like T1 is nothing but Al_2LiCu or Al_6CuLi3. So, these are the kind of precipitates.

So, this is T2 this is T2 and here we have certain amount of copper. So, these precipitates from along the grain boundary, ok and that makes this grain boundary activity higher than the surrounding grains. Now, interestingly in this case the dissolution of precipitate does not happen dissolution of precipitate does not happen. Then what part dissolves? The depleted chromium narrow zone along the grain boundary that dissolves, ok.

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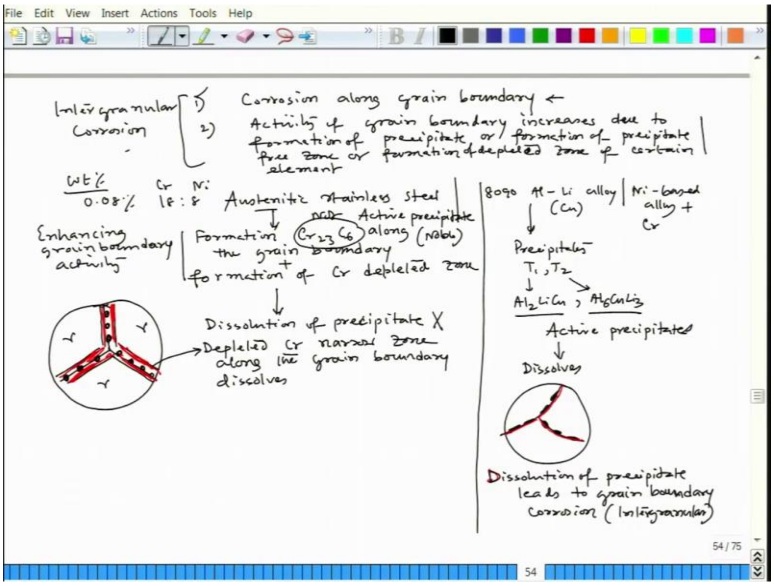

Intergranular Corrosion
1) Corrosion along grain boundary ←
2) Activity of grain boundary increases due to formation of precipitate or / formation of precipitate free zone or formation of depleted zone of certain element

wt%
0.08% Cr Ni 18 : 8 Austenitic stainless steel

Enhancing grain boundary activity

Formation $Cr_{23}C_6$ along the grain boundary + formation of Cr depleted zone

~~nob~~ Active precipitate (Noble)

Dissolution of precipitate X

Depleted Cr narrow zone along the grain boundary dissolves

8090 Al – Li alloy (Cu)

Ni-based alloy + Cr

Precipitates T_1, T_2

Al_2LiCu, Al_6CuLi_3

Active precipitates

Dissolves

Dissolution of precipitate leads to grain boundary corrosion (Intergranular)

So, if you see let us say this is austenitic stainless steel; that means, the entire steel and the carbon content let us say 0.08 percent and this is 18 percent chromium and 8 percent nickel and these are all in weight percent and for your information whatever composition I would write they will be all weight percent; if I do not mention specifically these are in atom percent otherwise everything will be weight percent.

Now, in this case what happens? This is the grain boundary of austenite in this case this is austenite and this chromium carbide precipitate happens along the grain boundary and due to that surrounding region this region become depleted with chromium and then that is what the dissolution happens in this zone; in this zone.

But, here interestingly these are active precipitate, fine. In this case this one is not active precipitate active precipitate not active precipitate rather these are noble precipitate. Why noble? Because it does not dissolve, if it is active precipitate, that dissolves. So, here these dissolves and if you have a aluminium grain grains this is aluminium this is one grain, this is aluminium, lithium, copper, alloy grain.

So, this precipitates happens along the grain boundary and actually what happens? This precipitate dissolve and that is what the grain boundary happen attack happens. So, that is what the dissolution of precipitate leads to grain boundary corrosion or we can say intergranular corrosion, ok. So, if you see these two different cases the situations are different, but entirely see all both the cases the dissolution is actually happening along the grain boundary.

So, the first condition is met, but the second condition that is grain boundary precipitate which leads to depleted zone of certain element or those precipitate itself would dissolve and that leads to a rapid grain boundary corrosion along through the body of that particular material. It does not stay on surface, ok.

It goes deep into the material and, but if you see the mild steel there also the grain boundaries are actually getting evolved due to a preferential attack of the grain boundary. But, there the second condition is not meeting. So, that is what we do not term it as intergranular corrosion though grains grain boundaries are visible due to grain boundary attack.

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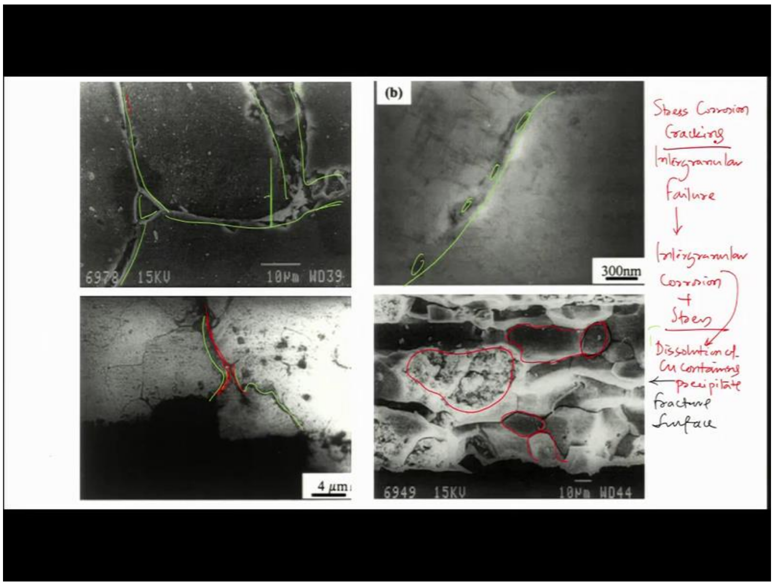

Stress Corrosion
Cracking
Intergranular
Failure
↓
Intergranular
Corrosion
+
Stress
Dissolution of
Cu containing
precipitate
fracture
surface

Now, coming to some of the examples let us see if in this case ok, so, let us go to some of the pictures. So, this is one such picture I just wanted to show you, fine.

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So, this is our work. You can go to this particular paper and this is actually work done at IIT, Kharagpur. So, this I am also the active member of this work. Now, in this work we worked with a titanium, aluminium, lithium 8090 alloy and there aluminium is 2.29 percent, lithium 1.59, copper 1.2, magnesium 0.08, a little bit of iron 0.08 and little bit of silicon 0.07.

Now, that alloy was actually solutionized at 170 degree Celsius solutionized and etched that 170 degree Celsius. And, during etching after etching we have done stress corrosion cracking test. Now, on the stress corrosion cracking part let me tell you what we did there are many modes of this corrosion cracking. One is constant load, another one is slow strain rate test machine. So, in case of constant load we will put load much lower than the yield point of the material and then hold it there in the solution ok.

And, in another case flow straight slow strain rate test or we call it SSRT there we strain the material at a very very low strain rate of the order of 10 to the power minus 6 to minus 7 per second, that is the strain rate we provide and that low strain rate allows the material to interact with the solution so that the corrosion as well as straining happens in parallel.

So, there are modes of quasi static corrosion tensile test where the strain rate is of the order of 10 to the power minus 3 to 10 to the power minus 4 per second where the test duration happens in case of mild steel if you do it will happen maybe for a half an hour and then it will break. So, which is fairly high degree of straining but, in case of slow strain rate test where if you put 10 to the minus 6 strain rate, it can continue for a 3 days that testing can continue for 3 – 4 days.

So, that means, why it is stress corrosion we will come to see that stress corrosion part that is stress plus corrosion that is what the both the effects will be felt and in case of stress corrosion cracking we allow that slow strain rate, low strain rate because the corrosive solution also has interactions with the grains and grain bodies, grain boundaries so that we can sense what is it is what is the material sensitivity to a stress corrosion cracking in a solution.

Similarly, in case of constant load testing we hang the material giving a constant load which is calculated on the basis of the yield point of the material and then leave it in the solution. If you take 50 percent of the yield point load or let us say 70 percent of the yield point load depending on the severity of that corrosive media the material at some point time will fail, ok. So, there we do not get the elongation part, but at least we could sense what is the degree of corrosion stress, corrosion attack.

Now, this alloy what we did we did constant load machine and this is the ACM pictures after the testing after the constant load testing we have tested it is we have taken a micro graph and then started taking the picture out of it under ACM and we show that these are the grains sorry, these are the grain boundary ok.

These are the grain boundary fine and interestingly you could see that these are the kind of corrosion deposits because when straining happen the corrosion is happening and then corrosion products are getting deposited there because after it breaks for example, today morning it breaks today tomorrow morning when I come that time I see that there the sample has broken in that mean time it has also gone under corrosion.

But, at the same time let us say the breaking is taking place is a crack propagation, but it crack propagation might happen slowly. So, by the time crack propagates out completely there could be corrosion staff which is deposited along the corrosion points. So, that means, here you could see that corrosion points are basically nothing but those intergranular regime region.

And, if you see the 10; if you see the TM picture this is a brightful picture. So, there you could see those are the these are the basically precipitates and these are forming along the grain boundary. So, this is another grain boundary and we have seen that the grain boundaries are having tight copper riched; copper rich precipitates because when that T 1 or T 2 that T 1 dissolves because it has copper, aluminium and lithium.

And, lithium and aluminium being active elements they dissolve due to de-alloying effect and there would be left out copper. So, copper enrichment happens around the grain boundary. We have done that ACM EDS and we could see that along the grain boundary after corrosion failure we could see that the grain boundaries are having lot of deposits of copper.

So, the initially the copper content was around this was in the material it is 1.59, but along the grain boundary we could find even 70 percent copper. So, that means, that copper deposits happens because the copper rich precipitates are actually dissolving and this is also classic case of dealloying because aluminium and lithium both are active compared to copper.

Aluminium, lithium goes to the; go to the solution in the form of ions copper leave, copper is left behind and that actually deposits there and then that is what we are getting increase copper content, fine. And, if you see another mode this is optical micro graph all of after fracture wherever fracture happens after fracturing we have checked the cross section of the fracture and then polished and took a micro graph and it is also if you see that it is actually attacking along the grain boundary. So, these are along grain boundaries.

And, here the copper deposit shows and proves that it is actually dissolution of copper rich, copper containing precipitates into the solution leaving copper there. So, it is a basically the mechanism is dissolution or active precipitates there and those precipitates are forming along the grain boundary and that is what the grain boundary attack is taking place or intergranular attack is taking place.

And, since we are putting stress along the tensile axis and because of the stress and straining it fails and because of the failure the fracture surface become intergranular also. So, this is the fracture surface. This is a typical fracture surface. This is a typical fracture surface and interestingly, you would see that as if those grains are pulled apart from their facets. So, you could see the grain facets. So, this is one grain facets so this is one grain facets you see. So, this is a grain facets. So, this is another grain facets, fine.

So, this faceted structure can be easily visible under the fracture surface after that intergranular, after that stress corrosion cracking and this particular feature that is the intergranular of the faceted micro structure also proves that it is basically intergranular corrosion plus stress which lead to stress corrosion cracking, fine.

So, we could see that the why the precipitates are dissolving and then having intergranular corrosion and since it is also pulled and that pulling effect the pulling has its effect to disintegrate those grains along the facets, along the boundaries and that is what you could see all those facets grain facets and this is basically nothing but corrosion deposits.

So, this is a typical intergranular failure and that happens because of intergranular corrosion plus stress and intergranular corrosion relates to the dissolution of copper containing precipitate precipitate which are active precipitates; because if it is active they dissolves and that is what we have intergranular corrosion plus intergranular failure due to stress corrosion cracking.

So, I just thought I should give some example. So, this is one typical example. This is actually let me tell you I have worked during my masters, ok. So, this is one work I wanted to show you which gives you and understanding that why intergranular corrosion happens and what it is; it its implications because it implication is stress corrosion cracking happens intergranular mode and remember stress corrosion cracking is a very very deleterious mode of failure of materials.

So, let us stop here. We will continue discussing intergranular corrosion in our next lecture.

Thank you.