Corrosion Failures and Analysis
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Lecture - 41
Stress corrosion cracking: Mechanism (Part 3)

Let us start lecture 41 and the course is Corrosion Failures and Analysis. And, we will continue our Discussion on Mechanisms of Stress Corrosion Cracking.

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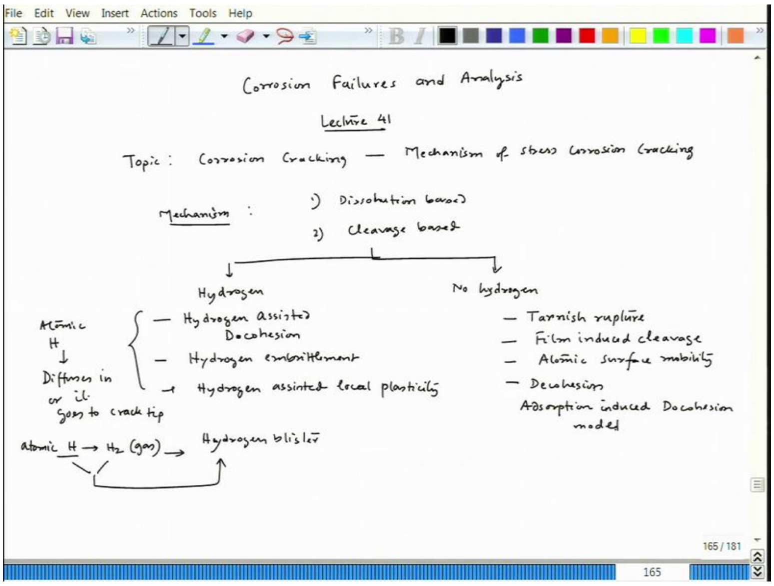

So, the course is corrosion failures and analysis, corrosion cracking and in that we will talk about mechanism of stress corrosion cracking. And, in fact, while doing while understanding mechanism of stress corrosion cracking, we will also talk about hydrogen induced cracking or hydrogen assisted cracking as well as corrosion fatigue.

Now, we talked about in the mechanism part, we have two major mechanism; one is dissolution based, which either can be preexisting path mechanism. And, otherwise it could be film rupture model or slip step model, as well as there could be possibility of tunnel mechanism. In all the cases all those cases dissolution initiates the crack as well as you have the stress coming in which allows the crack to keep opening up.

So, that is the dissolution based and we talked about that in previous lecture. The second one is cleavage based, which leads to cleavage fracture surface. Now, that has 2 segments as we have talked one segment is there are 2 segments; one is related to hydrogen, another one is where no hydrogen is involved. And, in fact, when hydrogen is involved we have several other categories; one is hydrogen assisted decohesion model, hydrogen assisted decohesion.

Then, we have hydrogen embrittlement, then hydrogen assisted local plasticity. In all those cases we need atomic hydrogen; atomic hydrogen which somehow diffuses in or it goes to crack tip ok. So, that is the atomic hydrogen is involved, the another kind of hydrogen related cracking is observed which is called hydrogen blister. So, this typically should not fall under this ssc, but it also involves hydrogen related cracking of the material.

In fact, it leads to a kind of fish mouth kind of failures appearance or it also leads to a kind of delamination. Now, here we do not have do not involve see it is basically both atomic hydrogen, that is involved and that atomic hydrogen when it converts to hydrogen. So; that means, this gaseous hydrogen. So, this combination of these two it is actually give rise to hydrogen blister ok, we will talk about that, so, this where hydrogen is involved.

And, where no hydrogen is involved there are couple of mechanisms. For example, one is of course, tarnish rupture. So, then we have film induced cleavage mechanism, then there could be possibility of atomic surface mobility model, then we can also have it is basically we can say decohesion model. So, where other than hydrogen comes in.

So, this has a name to its name called adsorption induced decohesion. So, these are in broad sense these are some of the models which addresses cleavage based scc ok and all those cases except here.

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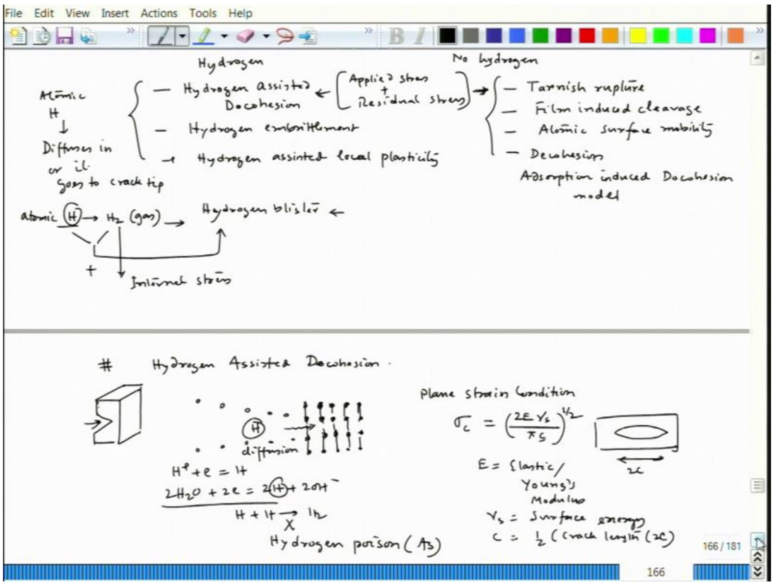

We must be having applied stress or residual stress. So, this is important in both the cases, both the cases. But, here the stress generates because of this hydrogen. Hydrogen actually leads to the stress which is internal stress. So, that evolves when we have hydrogen blister, but since this hydrogen comes from corrosion product and even though it is internal stress which is coming due to hydrogen.

So, but now since corrosion as well as stress is involved, we can say that this is also a partially stress corrosion cracking where the stress is evolving, because of hydrogen gas formation inside the material. Now, coming to the explanation if we talked about, if we talk about hydrogen assisted cracking hydrogen assisted decohesion.

What happens? If you have a crack let us say this crack is there and this is a crack within this crack I have just drawn this is a crack. So, in this portion I have just drawn a schematic atomic arrangement. What happens this atoms are bounded together, this bounded together ok. Now, here all the atoms are present in that metal.

So, these are bounded ok. Now, what happens? Hydrogen goes in. And, that hydrogen formation can be possible if it is acidic medium, then this hydrogen can form or if it is water reduction. So, these two reaction can give you atomic hydrogen and if there are hydrogen poison like arsenic phosphorus. So, those kind of stuff they have actually act as hydrogen poison ok. So, those hydrogen poison would not allow this recombination reaction.

$$H^{+} + e = H$$

$$2H_2O + 2e = 2H + 2OH^{-}$$

So, this reaction does not allow like arsenic ok. So, when that poison is there so, that atomic hydrogen will not combine and form hydrogen gas. And, this atomic hydrogen is very small size atom so, that can diffuse in. So, this is diffusion of hydrogen atom, in the in the metal at the crack tip.

And, when it diffuses it actually reduces the fracture stress and in the plane strain condition. In the plane strain condition you can see this is fracture stress which can be related to the formula 2 e gamma s divided by pi c half and this c is basically the half of. So, if this is a crack in a body and this is the crack length which is of 2 c. And, then E is elastic modulus and gamma s is basically E is elastic or Young's modulus.

$$\sigma_c = (\frac{2E\gamma_s}{\pi c})^{1/2}$$

And, gamma is the surface energy and c is half of the crack length of 2 c is basically the crack length and this is known as Griffith equation.

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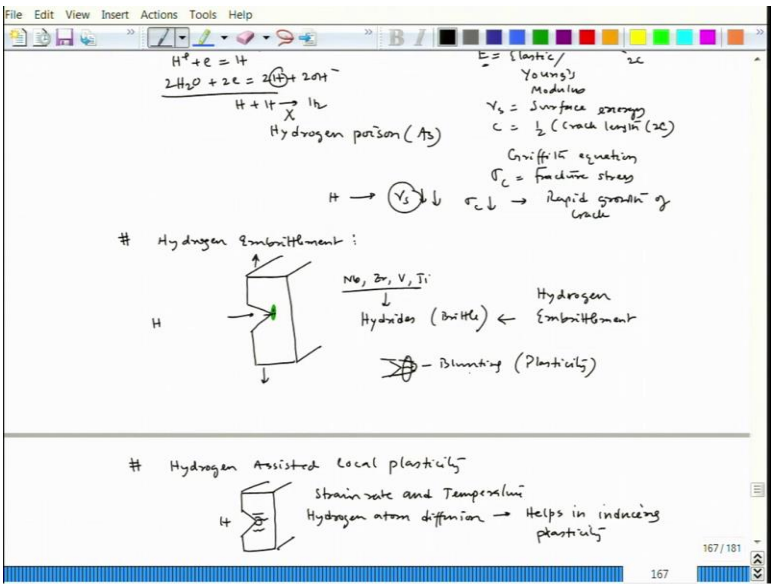

Now, this is the fracture stress this is now when what happens this hydrogen reduces the gamma s. This hydrogen gamma s reduces because of the hydrogen diffusion into the material, it actually reduces the inter atomic forces. So, that if this one reduces, then e is material property.

So, now, this sigma c which is basically the fracture stress and if this reduces, then fracture stress also reduces. And, that would lead to rapid growth of crack ok. And, this happens because the stress that is required for failure of that material, it happens at a much lower stress.

So, this is the this is actually as per this hydrogen assisted decohesion model, where fractures rapid growth happens due to lowering of surface energy. And, that happens due to decohesion between 2 atoms the bond decohesion ok. So, this is the hydrogen assisted decohesion.

So, there could be model like hydrogen embrittlement. In hydrogen, in hydrogen embrittlement, what happens this is the crack tip, this is a crack tip. And, in that crack tip we have hydrogen generation atomic hydrogen, which is either by hydrogen atom reduction of hydrogen ion or reduction of water.

So, these hydrogen can diffuse in ok, when it diffuses in then if there are hydride forming elements like, niobium, zirconium, vanadium, titanium. So, their hydrides form. So, these hydrides are extremely brittle. Now, if let us say this hydride forms. So, this is the hydrides. So, let us say this is my hydride that has formed around that zone. What happens? This crack tip has go, because it is a brittle and this is under tensile stress this crack can progress through this.

So, now if this is my hydride and the crack tip is here, the crack can progress through this. And, once it reaches to the softer matrix; that means, the away from the little once that crack has moved through the hydride and it interacts with the softer tough matrix. So, there this crack tip will get blunted.

So, this crack has moved like this and it has got blunted. So, this blunting happens, because of plasticity or deformation of the crack tip. Now, again the second level of hydrides form, because hydrogen keeps diffusing in. One hydride layer is broken the second hydride layer forms and then again crack moves, till the end of the hydride and it experiences softer matrix deforms and then blunting happens crack stops.

So, like that way the crack moves into the material. So, this is actually since it is a associate with hydrides, which have brittle phase that is what it is called embrittlement. And, this is associated with hydrogen that is what it is actually or hydrogen embrittlement.

So, this is another mode of failure when we have hydrogen. Now, there could be possibility of hydrogen assisted local plasticity. Now, this is a crack tip again this is the crack tip. And, here at some level of strain some strain rate and temperature, this hydrogen goes into the material diffuses into the material.

So, this is a diffusion hydrogen diffusion hydrogen atom diffusion rather. And, due to the diffusion it actually reduces this particular force this actually leads to a plastic zone. This hydrogen diffusion helps in inducing plasticity ok. So, there and if it is plastic then definitely deformation would happen and the deform zone can also get dissolved, because that is active zone. So, that way the crack gradually progresses due to this hydrogen atom diffusion and that leading to plastic zone creation.

And, that happens in a very local situation around this zone and that zone is getting deformed due to the triaxiality of the stress at the crack tip. Now, this is not embrittlement because rather it helps in making the material plastic.

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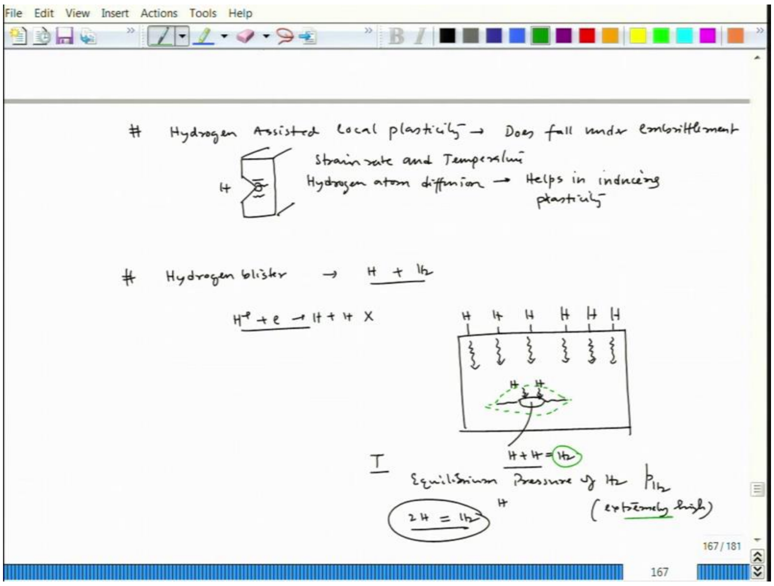

So, this does not fall under this is, this particular thing does not fall under, does not fall under embrittlement. So, this is another model proposed. Now, we have hydrogen blister. In case of hydrogen blister as we have discussed before that it is associated with hydrogen plus hydrogen gas.

Now, in the previous three cases we do not have hydrogen gas related problem. Now, what happens if let us say some container is holding, let us, say a steel is holding acid. And, there could be possibility of enormous amount of cathodic reaction, where hydrogen it forms hydrogen atom and if this recombination is not possible.

So, then through the metal; through the metal, so this hydrogen this hydrogen will start diffusing in. And, since its a small atom it is easy to have diffusion. Now, if there are internal flaws, let us say this is a internal flaws. Now, hydrogen is also reaching there and that is also diffusing inside the void. Now, inside that void, hydrogen can combine and then form hydrogen gas. So, gradually this hydrogen gas buildup will takes place inside the void. And, now we have at that temperature because equilibrium is temperature function.

So, then we have the equilibrium pressure of hydrogen. So; that means, p H 2 in equilibrium with hydrogen ok. So, now, I have I can write this ok. So, this reaction would require to reach equilibrium, and the pressure that requires for this equilibrium to establish that pressure would be several 1000 extremely high, extremely high, several 1000 several 100s of atmosphere. So, because of that huge pressure created within this small volume that wave voids. So, that crack extends ok.

So, now, it appears a kind of fish mouth kind of crack like this ok. So, this crack is actually observed mostly on the outer surface, not internal surface rather on the outer surface. So, this particular crack you could see that its not due to external stress. Rather the stress is coming due to extremely high pressure and that pressure leads to internal stress, which leads to a failure of the material.

So, this is hydrogen blister, where hydrogen diffusion and then recombination of hydrogen takes place. And, now question is this free. Once it is recombined to once it is combined to H 2 and that H 2 will not be able to push through the material to the matrix of the metal. Because its molecule needs a bigger molecule it cannot push through.

So, then that hydrogen is actually getting accumulated inside the small void and since it requires a very extremely high equilibrium pressure, that is what the pressure builds up happen, where pressure buildup happens, inside the small cavity of void and that leads to fish mouth kind of failure. So, this is hydrogen blister fine. So, you can see that its bit different than previous three cases where the stress is already there either it could be residual stress or it could be applied stress.

But, in this case residual stress is also not there applied stress or it could be also in under applied stress, but mostly it is not within this applied stress or residual stress even if you start with the perfectly and yield one. Then, also this kind of failure happens hydrogen blister happens, because of this extreme internal pressure buildup due to hydrogen gas inside a void. So, this is hydrogen blister. Now, if we come to other and this all those fractures actually leads to all those cases, it leads to Tran's granular cleavage failure.

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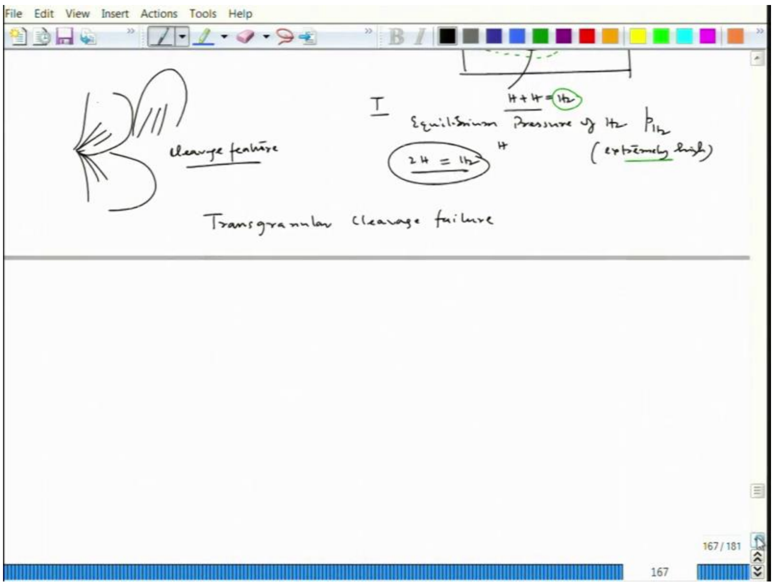

And, the surface looks like kind of radiating kind of surfaces. So, this kind of appearance one can look at without having a specific grain facets. So, this is typical cleavage feature, you can also go to net and then have a look at it what is that the look of cleavage feature.

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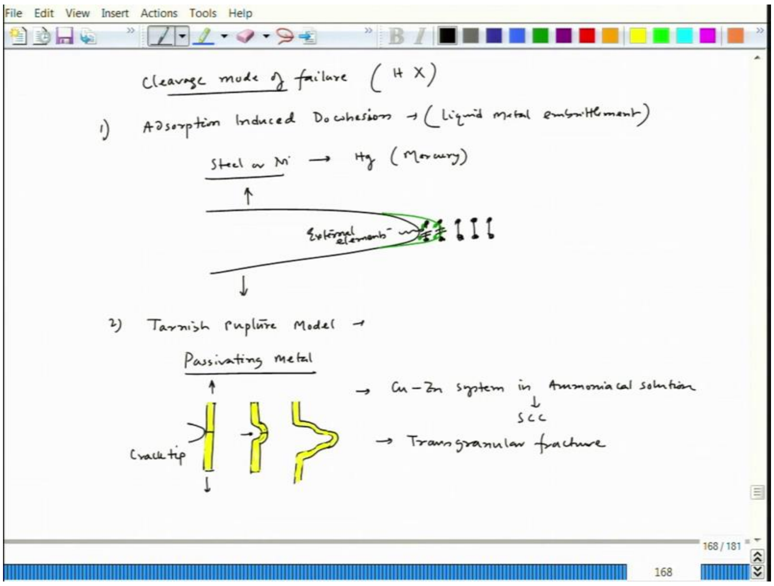

Now, coming to other cleavage mode of failure, so if we talk about cleavage mode of failure so, there where hydrogen is not involved ok. So, the one can think of just like decohesion model, the hydrogen decohesion model, where hydrogen is actually reducing the bond strength or the surface energy. And, if surface energy reduces then fracture stress also reduces as we have seen in case of hydrogen induced decohesion model.

Then, here also there could be possibility of decohesion, we call it adsorption in induced, in adsorption induced decohesion. Now, here this could be possible in case of liquid metal embrittlement, liquid metal embrittlment. For example, if steel or nickel alloys are kept in or stressed in mercury, then this kind of defect can be observed. Then of course, you can have it in nickel bismuth system, aluminium gallium system; that means, the gallium is the liquid metal copper Hg system mercury system.

So, what happens? You have this crack tip ok and those atomic bonds are there. So, this is the atom these are the atomic bonds and this external agents, I would say external elements or external elements, they can diffuse in and weakens this particular bond strength and this bond is broken. So, these are in this cases here also the crack so, if this bond is broken.

So, these bonds are broken due to this external elements which is coming and sitting over there. So, it is sitting over there. So, like this so, this green colors are let us say external elements. And, then this failures happen this bond breakage happen and then this fracture surface or the crack grows here like this. So, like that way the crack grows into the material and of course, there is a stress which is their across the crack ok.

So, this is adsorption induced decohesion model ok. Now, there could be possibility of tarnish rupture tarnish rupture model, what happens? This happens in case of passivating metal; in case of passivating metal can we stop, ok. And, when a metal let us say metal surface.

So, this is the metal surface let us say, and let us say this is this is the passive layer ok. Now, there could be possibility of this there is a stress there is a stress acting. And, now when stress happens? So, then the crack tip is here ok and this is the crack tip. And, because of the triaxiality in that crack tip there could be possibility of a crack growing in and when crack grows in.

So, then the appearance would be. So, this is the crack which has gone in and now since it is a highly passivating metal immediately it passivates this portion, this portion passivates ok. Now, in the second time again that crack again moves in. So, this is passivating ok. And, the crack again moves in this crack moves in again that so, after that. So, now, again that particular surface would be forming passive layer. The stress all the time what it does it allows the fracture to push through the brittle passivating metal.

And, then once it reaches to the base metal the p crack growth stops and then again the fracture happens in that film and then that cycle continues. And, in that way the fracture surface or the crack tip grows in or the crack grows into the material. So, this is the tarnish rupture model, which can effectively analyze the fracture happens in case of copper zinc system or let us say brass in ammoniacal solution.

So, this kind of scc observed and this is the typical scc and for example, if you recall we talked about season cracking of brass casing of bullet early what used to happen in early 90s 1900.

So, that has been solved by removing ammonium removing residual stress at that cream portion, but that mechanism how it grows that can be explained through this? Now, it actually typicals talks about Tran’s granular stress as Tran’s granular fracture, it typically talks about Tran’s granular fracture, but many a times in some systems we could observe inter granular feature also.

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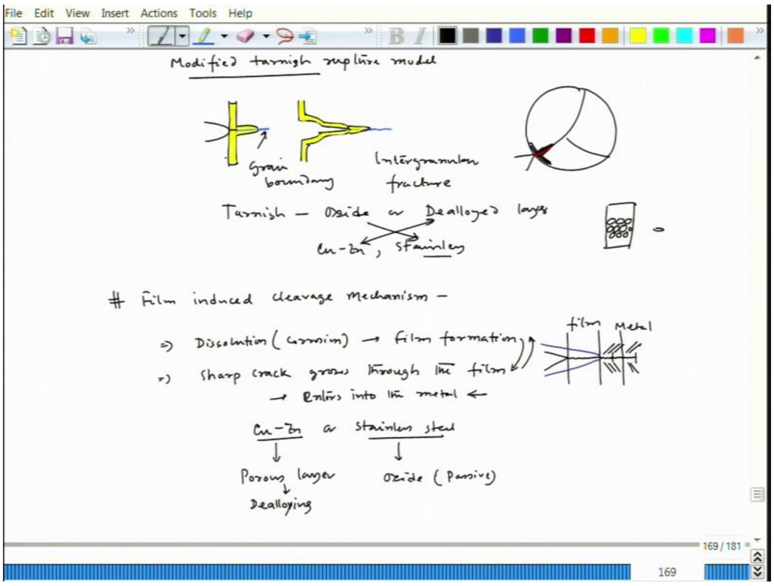

So, in order to address that, so, there is a modified tarnish rupture model ok. So, in that case what happens? This feature what is there in the beginning we have the same operation going on so this is the film ok. And, this film we have a crack that is going in and that crack will lead to a small fracture here in the film. And, then the film will grow into the and let us say there is a grain boundary.

So, let us say so this is the grain boundary ok. The film will grow into the grain boundary. So, this blue color let us say I am changing the ok. So, this film is growing into the blue color, this is the film growth ok and this is the grain boundary. So; that means, here the film is actually if we have a grain structure like this. Let us say this is a film thin film and that film is growing through the grain boundary and if this crack is coming here.

So, that crack will grow through the grain boundary. And, in fact, through the film and actually if it is going that crack is moving through the tarnish layer actually it is moving inside the grain boundary. So, this way and then second time when it happens so it has grown like this and second time this will go so this is actually when the crack has moved little bit.

So, now, this film again will grow inside along the grain boundary. So, this is the grain boundary this is the grain boundary like that way, the fracture moves along the grain boundary. So, this blue color is basically the grain boundary. So, when it happens then definitely it would lead to inter granular failure surface fracture surface. Since, fracture is taking place through the grain boundary. So, this is a modified tarnish model, where this at times if inter granular fracture is observed. So, then this can address that particular process.

So, if for example, if this particular section is dealloyed section so there is a small small pores, because of the dealloying. And, now you could see that if this pore size is few nanometer that the sharpness at the of the crack tip can be imagined ok. So, that is what this is and that is what this is possible in case of copper zinc alloy, where dealloying is absorbed, even it can be if it is stainless steel, there also this kind of tarnish rupture mechanism can be possible, where in case of stainless steel.

So, this is de alloying case and this in this case in case of stainless steel it could be oxide formation on the surface. So, this is tarnish rupture model. Now, another model which is there that is called film induced cleavage mechanism. Now, in this case first step is dissolution or corrosion, which leads to film formation.

And, then the sharp crack grows through the through the film, since the film is brittle. In fact, when the sharp crack grows through the film, it actually enters into the metal matrix into the metal. So, now, it does enter into the metal, but before it grows fast into the metal since the metal is ductile. So, the crack arrest is possible by local plastic deformation and blunting can happen crack blunting can happen.

So, this is actually in this case just it enters through the film the crack does not stop, that is the only tricky part here, it also enters into the metal. So; that means, you have a film you have a film and this is the crack and that crack grows through the film. And, now in that film also away even after entering into the end boundary of the film this is the metal part, this is the film; it also enters little bit into the metal. And, of course, in that metal there will be slip planes so, the deformation can happen and then the crack is arrested over here.

So, once the crack is arrested the crack will move into the material. So, the second step is the crack moves into the material like this. And, then the another film will form so here the film forms again, another crack grows in crack grows in and then it also enters into the metal and then the deformation again happens and the crack stops here. So, like that way it happens it actually continues in this cycle.

So, its basically film leading to sharp crack growth and the crack growing little bit of crack, which is growing into the metal and then it stops due to blunting or plastic deformation at the crack tip and then the film formation again happens. So, that cycle goes on. So, this is the cycle. So, now, another this is now first is this one and so this two processes will continue and then gradually the crack grows into the metal.

So, this is film induced cleavage mechanism and this can explain the crack in case of the crack with the scc in case of copper zirconium sorry copper zinc, copper zinc or stainless steel. So, there one can explain this and that case in this case the film could be porous layer and that porous layer is forming we have already seen dealloying, because of the dealloying. Since, the dealloying creates very small tiny nanometric size pores. So, those pores can combine with the growing crack, and that can make a very sharp nature of the crack tip.

And, in case of stainless steel it is basically oxide layer which is the passive layer. And, that oxide layer could be highly brittle and that brittle oxide layer can be cracked open by the growing fracture point. And, then a growing crack point or crack tip And then this two things happens in cycle. So, that way this film induced cleavage mechanism can be explained.

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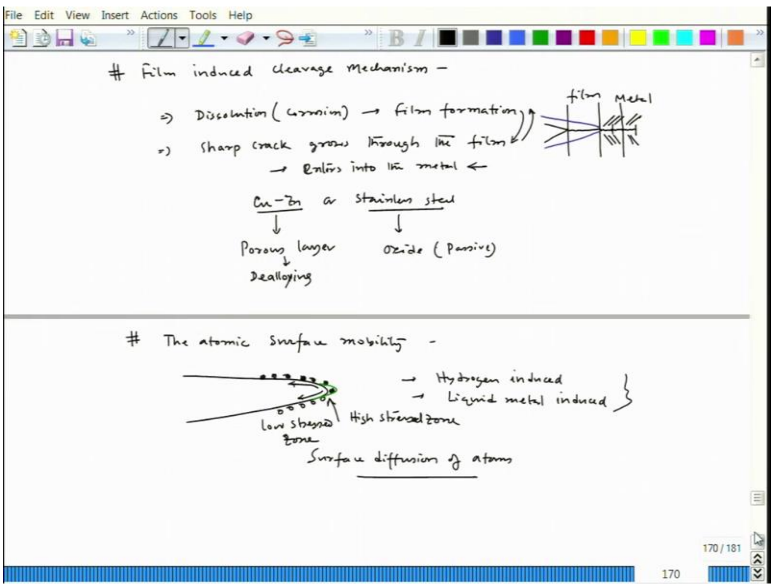

And, the last one what we can you can thought of is basically the atomic surface mobility mechanism. In this case some of the species in this in the corrosive media. So, this is the crack tip and these are the atoms at the crack tip. And of course, the crack tip is basically high stress zone and away from the crack tip is low stress zone, low stress zone.

Now, what happens? Because of those species basically low melting compounds it forms, then these atoms would like to this metal atoms would like to move away from the high stress zone to the low stress zone. So, these atom is moving, this atom is moving from high stress to low stress. And, when it moves then this crack grows little bit. So, like that way, this cycle goes on because of that those surface diffusion happens the atomic atoms moves from low stress to high stress and that happens due to surface diffusion surface diffusion of atoms.

So, this is basically the atomic surface mobility. So, this way the crack surface or the crack point moves into the material. This is another model that is that exist and it can be either hydrogen induced or it could be liquid metal embrittlement or liquid metal induced ok. So, that way this surface atoms of the metal would move away from high stress to low stress and since crack tip is at a high stress zone. So, the crack tip moves into the material and that way final failures happen in that material. So, this is atomic surface mobility.

So, these are in nutshell the some of the mechanisms that are available to address scc or the stress corrosion cracking behavior of metals and alloys. Now, we are left with two more important aspects; one is fatigue corrosion or corrosion fatigue. And, the second part is what are the protective routes or protections, what we can think of to mitigate stress corrosion cracking or fatigue cracking not fatigue cracking rather it is a corrosion fatigue.

As well as hydrogen induced cracking or hydrogen assisted cracking. So, those part we will take up in our next lecture.

Thank you.