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Present

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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Lecture 32

Broad Subject: Stress corrosion cracking: mechanisms(dissolution controlled)

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So we see that residual stress or built-in stress in the material that is very important aspect and that can lead to stress corrosion cracking because that residual stress acts as static tensile stress within the material and if you have a corrosive action then you can have SCC or Stress Corrosion Cracking and also we see that the residual stress could be dangerous or would be disadvantageous as well as advantageous. One advantageous example of residual stresses when we go for short pinning we introduce compressive stress at that compressive stress basically prevents fatigue failure. So this is one advantage of residual stress. We actually incorporate compressive residual stress. That we have already discussed and the way in order to for example if we have a tensile component of residual stress or built-in stress or dead load that the residual stress could be removed by low-temperature handling and that low-temperature stress relieving operation if we do that time we can see the residual stress can be removed.

So the residual stress is one issue and then second then – other stresses for example tensile stress due to loading action okay and that would be there while material has stress corrosion cracking is develop, stress corrosion cracking is developed in the material that time there of course the action of tensile stress would be there.

Now there are are some of the features which are important to mention in case of stress corrosion cracking of materials, SCC, if we would like to see. The features one is generally the experience says that pure metal are more or less immune to SCC. SCC or resistant to SCC. So generally we see in case of alloy systems more frequently compared to a pure metal but of course the pure metal also can experience stress corrosion cracking but it would take a long time to develop that stress corrosion cracking.

Now second case of course existence of tensile -- static tensile stress. That is important, and moreover whenever a material is experiencing stress corrosion cracking that time we generally see that there is one threshold stress, stress value that is to be overcome or that has to be exceeded so then only we see the stress corrosion cracking for a particular material. So the material, depending on the material character or the mechanical behavior or the solution that is in which the material is being exposed to so that case the threshold stress can vary accordingly. Now then we have SCC definitely the environment is important issue. The kind of environment that the material is exposed to depending on that the stress corrosion can happen or it may not happen. Then we have the whenever we have stress corrosion cracking if we do some experiment let say if we supply cathodic current to the material let us say our material is under load and stress. This material is under static tensile stress which is below the deformation stress or the yield stress of the material, that time if we supply let us say cathodic current so then we see that the stress corrosion tendency or the stress corrosion cracking tendency goes down. So we can prevent stress corrosion cracking or linger the stress corrosion cracking in a particular material if we supply cathodic current and on the other way around this case, the SCC is somewhat prevented or it took or it takes long duration but same way if we supply anodic current that time it actually accelerates the stress corrosion cracking. Stress corrosion cracking tendency increases. So that suggests that the stress corrosion cracking is also electrochemical in nature. That means the electrochemical dissolution or the amount of electron in the material, excess electron in the material what sort of reaction that is going on on the surface whether it's anodic reaction or cathodic reaction that can determine the SCC tendency of a particular material. So it's electrochemical in nature.

Then of course we have for example SCC crack has and with the action of combined action of stress as well as corrosion that is the static tensile stress the crack is gradually growing inside the material.

Now if you would like to see the crack growth rate so the crack growth rate for SCC, SCC crack growth rate should be lower than if you consider the crack growth rate of normal mechanical crack growth rate that means without the action of corrosion and if we only consider there is no stress but only the corrosion action or the dissolution itself can lead to a complete failure, complete breaking of this material let us say this block is entirely broken into halves due to the corrosion action itself so that time the rate of, I would say the crack, if there is one preexisting crack already there is one preexisting crack let's say so that crack is moving because of the corrosion action that and the rate of crack growth only corrosion. So this one would be in the middle of this two extreme position. This would be very fast. This would be very slow and this has some intermediate range of crack growth rate. So that means this is intermediate crack growth rate. So that means we have an intermediate crack growth rate of the SCC when the crack is moving due to the SCC phenomena.

Now finally there is whenever you have this material is breaking down into pieces so you will have some fracture appearance and the fracture appearance for example in case of normal mechanical growth if it is ductile fracture then it is involved with -- it is associated with the dimple fracture and if it is brittle fracture then it is basically a smooth cleavage fracture but in case of SCC you can have two kinds of fracture surface. Fracture surface one is intergranular or it could be transgranular fracture.

So now intergranular fracture for example if this is the material you have different grains. Now if we see the crack growth in the material then we will see the crack is growing along this particular grain boundary sections. So crack growth path could be like this. So it's basically intergranular in nature that means the crack is moving along the grain boundaries in the polycrystalline material and in case of transgranular material let us say this is my material where I have SCC crack and these are basically my grain boundaries and these are the grains. Now in that case let us say crack is there like this and that crack it may not take the path along the grain boundary. Rather it will take through the grain boundary, through the grain bodies. That time it is called transgranular that means through the grain body. So two types of cracks; one is intergranular, one is transgranular in a material you can have a mixture type of crack appearance. It could be intergranular plus transgranular both can coexist or it could be only intergranular in nature.

So for example in aluminum lithium alloy 8090 if we study the SCC mechanism SCC in that material, that case generally in that case we experience intergranular fracture and that time when the material is fractured like that then we will definitely see some sort of well-defined material facets, or grain facets so that itself talks about the intergranular fracture. So two types of fractures; one is intergranular, another one is transgranular and material when the material is under SCC there both the types can coexist.

Now once we understand the features of SCC let us get into the how the SCC can happen in a material. So that means what are the mechanisms by which can control the SCC. Now the third we will talk about mechanisms of SCC.

Now it has broadly categorized – it is broadly categories into two broad sections. One is, this one is it is basically a dissolution based mechanisms. dissolution based. The another one is cleavage based. Now in case of dissolution based as the name suggests that dissolution is dissolution due to corrosion that actually leads to crack initiation and the crack growth also will be decided by the corrosion dissolution. So actually here the corrosion initiates, corrosion leads to dissolution and that initiates crack and as well as the same thing would be active in growth process of the crack. Now that means the corrosion is initiating as well as the growth process of the crack is decided or controlled by dissolution. Now point is what does stress do there. So the stress action would be let us say we have a material, in that material we have a crack and now dissolution is taking place at this point and actually the tensile stress actually trying – it is trying to open up this crack and allow the solution to get into this crack tip so the further dissolution can happen. So this is the dissolution based model.

And then in the cleavage based actually this corrosion lead to embrittlement effect. Corrosion lead to embrittlement and due to the embrittlement the crack initiation can happen. So the crack that means the embrittlement part and the initiation actually the corrosion control or corrosion means it could be dissolution controlled or it could be some species or the product of corrosion reaction that could lead to embrittlement. So this could be dissolution based or let us say sometime hydrogen can generate due to cathodic reaction and that hydrogen let's say the material contains hydride containing elements and the stress assisted hydride formation could be possible for example, titanium, zirconium; those elements can form hydrides and those hydrides are brittle compounds and that and then at the crack-tip this is the crack-tip let us say this is my crack tip, at this crack tip hydride would form and that hydride leads to embrittlement at this point and there would be constant action of the stress and that stress within the stress level that the material is facing in the crack tip this hydride can lead to can break into pieces and then the crack can grow like this. So this embrittlement effect could be possible and now the point is the mechanical brittle fracture steps.

So embrittlement is happening. The crack is moving and the crack growth is controlled by mechanical fracture so propagation is controlled by mechanical fracture, mechanical crack growth but there also the corrosion could be effective. There actually corrosion can lead to – can actually activate this mechanical crack growth or the propagation step, corrosion can be very active and it actually helps in sort of catalytic effect it gives towards this mechanical crack growth. So then the growth process also, initiation of course the corrosion is important but at the same time in the propagation step corrosion also is helping by sort of making it catalytic effect. So these are basically two broad categories. One is dissolution base. Another one is cleavage based.

Now if we go to the dissolution based, only the dissolution based there are some different models. If you consider dissolution based models, one model is if you see the first model if that is talked about that is preexisting active path and then you can also have the strain generated active path. Then we can also have the corrosion tunnel model corrosion tunnel model and of course this corrosion tunnel model has been modified later on. So these are some of the examples of the dissolution based models. Strain generated active path also it has two subsections. One is called slip step dissolution model and another one is called film braking model, another one is called film rupture model, and then you have a slip step dissolution model. So these are basically different models which are existing and which are falling under dissolution based models. Let us first get to the preexisting existing active path model. Preexisting active path model let us say a material which is under stress and then the material is also exposed to solution and let us say these are the grain boundaries, and it is a polycrystalline material and that time the material can have active dissolution path along the grain boundaries. For example what we have seen in case of sensitized stainless steel, austenitic stainless steel there we see that there could be chromium precipitation along the grain boundaries and that chromium precipitation on the grain boundaries lead to chromium depleted zone around the grain boundaries and that chromium depleted zone is basically the active path for dissolution. So dissolution only will be concentrated along this grain boundary positions, grain boundary sides so the due to this rapid dissolution there could be a crack formation or there could be existing crack. Okay. So these crack gradually will move due to this action of stress along this grain boundary path. So this is a preexisting active path that means already you have some sort of a deposition or precipitation that lead to the grain boundary to be very active and their dissolution can happen and the initiation of crack can happen and then crack growth also will be decided by the rate at which the grain boundary is being dissolved due to the action of corrosive solution. And this one classical example for this is basically the SCC of stainless steel, intergranular fracture in case of stainless steel, stainless steel in pure high purity of water so or other environments. So this is one example for this kind of mechanism.

So here already and this can also happen in case of aluminum alloys. There the precipitation can happen along the grain boundary and that precipitates can itself act as the anodic sites where the dissolution of the precipitates can happen or in case of stainless steel precipitates are forming, those precipitates are not dissolving rather the surrounding areas around the precipitates those are dissolving. So aluminum alloys also it can happen and this is falling under active paths. It is preexisting active paths mechanism.

Now there could be strain generated active path mechanism. For example some cases some materials there you do not have this kind of situation where you have active paths already existing active paths let us in case of sensitized stainless steel where you have already active path along the grain boundary. If that is not existing then the strain generated active path can explain why the stress corrosion cracking happens in those materials. So the strain generated active path mechanism, strain generated active path there we have two varieties one is film rupture. Let us talk about film rupture case. Film rupture case in this case let us say a material is already having a crack and then you have stress action. Now this is the material and now this material is already having a passive film over the surface and also at the crack-tip passive film is forming. Now due to the strain action there could be this stress action can – will try to open up this crack and when it tries to open up this crack in this zone, this zone, the passive layer of the oxide layer that is under stress and there deformation, due to deformation that could rupture. So this part in this section the passive film would rupture and due to this rupturing action there this fresh metal surface which is exposed to the solution in this side there are solution. So the solution this part is exposed to the solution and due to this exposure there the local dissolution can happen.

Now this dissolution case local dissolution will carry on until and unless the another passive film forms for example local dissolution let us say the crack has grown up to this. So then again the passive layer would form. Now then again the fracture would be, the crack growth would be minimized or stop for momentarily until and unless this passive layer is again broken due to the action of stress. So now the point is now if this passive film generation or the rate of a repassivation and the rate at which rate of dissolution these are two important parameters. Now if the rate of dissolution is more than rate of a repassivation then the crack growth would be very fast because of the dissolution and if the repassivation rate is more than the dissolution then there would be lot of steps or lot of stoppage of this crack growth. So this depending on whether this is more than this or this is more than this, the crack growth rate would vary.

Now and due to this and this and whenever you have this rate of repassivation which is more than the rate of dissolution then the slip steps which would be generated and that would crack this passive layer which is repassivated layer due to the action of stress.

So there could be a slip steps like that then there would be this part can come like this. There could be slip steps like this so due to this action there could be breaking and there could be continuous dissolution. So this is film rupture case.

Now it could be slip step dissolution model. You can have slip step dissolution model and in that case let us say I have a crack like this and now the dissolution and there is also the existence of passive layer. Now due to the action of stress and the solution is at this end, due to the action of stress there could be slip and these are the dislocations and let us say for the simplicity we consider only the H dislocations. So along the active plane where the dislocation movement would be very easy there the slip would happen and due to this slip this part, so let me draw it in a bigger way, so let us say this is my crack and there is a tensile action like this. Now you have passive film formation. Now let us say this is the slip plane where I have my deformation due to the action of a slip deformation. So these are the edge dislocation which are moving along this easy moving path or the plane. Now due to this action this one comes down so this one let us say would be at this place at this place. So now you see this part is due to this slip it had happened and there will be break in the passive layer so you have this part which is exposed that is this part which is exposed to the solution. So here dissolution would happen and once dissolution happens then you have gradually this would match with this line. So gradually this would also try to match, try to match like this. So initially it was here now from that this part is out, this much is dissolution so you have this much growth.

Now this is happening in this way. This can also happen this direction. So actually finally if it is happening also this way so you have a sort of step. So this way the material has moved like this. So this part is out. So again this one match with this system and this one is matching like this. So this is out then. So gradually again this side would come to this much deformation would happen again. So this is exposed. This part again there could be possibility of this much is exposed and gradually you will see the crack nature would be like this. So it will form like this. So you have again this end you can have a active paths active slip plane. Here you can have this much is again exposed. So that way the crack is growing.

So this is called slip step dissolution model. A slip step is forming. This is the slip step and there the dissolution is taking place until and unless the passive film is again covering up. So this is growing like this. Now this slip step dissolution model you see that this point actually at this point or this point, this point until unless you have this passive film formation this is continuously growing and once the passive film forms until and unless the second slip step happens till then the corrosion is stopped or the growth is stopped. So that means you always come to see that there are some marks, arrest marks. Arrest marks. so arrest marks means until unless this part is covered up so it is moving once it is covered up with the passive layer the movement is stopped. So that place is basically called the arrest mark and this arrest mark always we come to see in case of SCC cracking. On the crack surface we always come to see this arrest mark and this can explain why the arrest marks can happen. Also the previous case also you can explain one can explain the why the arrest marks are coming because there also once the dissolution is taking place then once the crack-tip is covered up with the action of corrosion then also there would be stop in the crack growth. So these are basically arrest marks.

So we see that in case of slip step dissolution model we see that there could be arrest marks because of this crack arresting position when the entire thing is covered up let us say this part is covered up with completely then this part is not exposed until and unless another slip step which should lead to the crack in this section so dissolution further can happen. So you have actually the arrest marks. Now this can explain few things. One is why the transgranular fracture can happen. Transgranular fracture this process can explain because your crack propagation is not happening through the grain boundary rather it is happening on the slip steps what is being formed due to this dislocation movement. Now transgranular fracture it can explain but there could be some controversy for example in case of SCC metal we have the most probable path for slip step formation is 111 plane and that case 111 plane you can have the slip step formation, but actually the experimental evidence that says that the slip step is actually forming the crack propagation is actually happening through 110 or 100 so that is one controversy but it can explain transgranular fracture or transgranular SCC and second thing is though your crack growth is due to this dissolution basically actually rapid dissolution happens and that time you are supposed to get a very smooth surface because dissolution is happening and then passive film is forming. So the fracture surface should show a very smooth appearance without the presence of any features but actually on the fracture surface we see cleavage as well as and arrest marks and also – and sometime it also fails to explain why there is a very much matching opposing surface on the fracture surface, but it can explain many things, for example why transgranular SCC can happen in a material without having any active path, preexisting active path mechanism, as well as it can also explain why arrest marks can happen. So this is about slip step dissolution model.

We can also have one more model that is corrosion tunnel model. In this model actually for example if this is the crack, this is corrosion tunnel model. In this model let us say we have a crack like this and this is the crack and in that crack there could be in the crack section, there could be a sort of corrosion path where the active dissolution can happen and that would lead to – so actually this should be dotted because it is going inside the material. So this is the crack so these are the active regions for corrosion and then through that dissolution is very fast. So they are forming sort of tunnels in the cracked region into the material. So these are those tunnels and as it grows they are also growing gradually and finally we are – the material is having a very small section where the material are continuous are joined those small sections because of this action of stress the small space section can have normal mechanical failure.

So that means gradually this will be connected like this. So these are growing. These are gradually growing and finally you have this section where you have actual material connection. Rest of the section you have long tunnels and then since this is under static tensile stress this small fins or sections cannot withstand that much stress and finally they will have mechanical failure. So this is mechanical failure and this process can also actually in this zone where the mechanical failure is happening that section we would experience ductile fracture or dimple but actually in this zone we do not see dimple. So how to overcome this – how to modify this idea so that we can and this sections we have a cleavage nature. So not having any ductile fracture mode. So how to modify this entire model that is the tunnel mechanism so people have already modified this mechanism. So there they say that instead of having this spare tunnel they have initially the tunnel will form but later on this the tunnel will form a thin slits which is connected and there we have – this will go towards the level of atomic distance and this section will break and due to that we can overcome this ductile fracture or dimple mode, we can overcome – we can modify this system just a minute let me re-emphasize this part. So we see that those tunnels are forming and it is growing inside and they are growing also in the lateral direction and finally there will be thin slots that are left out and in that thin slot ductile fracture or dimple fracture can happen and so the final appearance would be -- final appearance on the surface would be like this. So like this that means these are those tunnels and they have grown and then naturally also they have grown and finally this much part is left out and because of the action of tensile stress there we have mechanical failure and dimple fracture or ductile fracture can happen on this zone which are the thin section where the material before cracking was under – was basically continuous body and there actually you have the connection of this material and because of this and those are thin sections and because of distance and stress those thin section will break mechanically.

So this sort of arrangement can be observed. This sort of mechanic – this sort of surface would be experienced and here we have a smooth surface of the groove nature and then you have this mechanical failure or dimple fracture zones. This is corrosion tunnel model, and the one modification to this model is and they are instead of making – having it spherical cross section this will due to the action of corrosive action as well as load they will become sort of elliptical nature and the thin and then this part will break and they will have this sort of appearance.

So this is the corrosion tunnel model and this is all under dissolution based model.

So this model can – this is also this dissolution based model can enable to understand why there is intergranular fracture that means the fracture along the grain boundary or why there is transgranular fracture and that transgranular fracture can be experienced, can be explained via film rupture model or slip step dissolution model and we see that the slip step resolution model or film rupture model we have arrest marks and that is one feature for the arrest marks - that is that a feature that arrest mark feature we can always – we can see on a transgranular fracture surface transgranular SCC or the space corrosion cracking sub fracture surface. So that can explain those why that arrest mark appears. We see that there would be a slip step that until and unless the passive film forms the slip step would go on dissolution but once the passive state forms until and unless there is a further slip step formation the crack is stopped.

So that way we can explain arrest marks. So this is the broadly we have the dissolution based models. Then we can talk about cleavage based model.

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