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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Lecture 33

Broad Subject: Stress corrosion cracking: mechanisms (cleavage controlled), factors affecting SCC, hydrogen embrittlement, corrosion fatigue

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So we have one more mechanism under the dissolution control mode, that is tunnel – corrosion tunnel mechanism. In this method we combine dissolution as well as mechanical failure; both the things are combined together and here what happens if you have a crack like this that time due to the corrosion effect in the crack-tip zone where you have slip steps, multiple tunnel forms due to corrosion. This is let us say the slip step zone where you have multiple tunnels, small-small tunnels and that are progressing inside the material. These are the tunnels and gradually those tunnels will grow and finally the material, the ligaments small-small ligaments will form, there the entire load will be experienced and due to the small cross sections of those ligaments the stress becomes very high and then it goes beyond the fracture stress UTS and then beyond the UTS and then the material fails by mechanical failure mode and so in these ligaments this small-small ligaments where you have – these are the ligaments, unbroken ligaments, there you might experience ductile failure because the stress goes beyond UTS and then the material fails as per the mechanical failure road, but we don't experience any ductile failure or dimple nature which is due to the micro-void creation and coalition.

In order to explain the matching surfaces which is the result of SCC, so this model has been modified and the modification says that the same micro-void this tunnel forms, multiple tunnel forms on the zone of slip steps, on the slip steps then those micro-voids instead of growing laterally uniformly, they form slots. Like those slots are forming and those slots are growing inside the material and finally you see that the fine and this dimension might reach to atomic dimension and there could be complete match between the fracture surface, between two fracture surface. So this is basically first stage you have a multiple tunnel formation and then simultaneous growth and then the breaking of all those ligaments due to the increase in stress of those ligaments on those ligaments and then finally you have mechanical failure on those ligaments and the modified versions you have, these are basically initially it was tunnel and then it was – it converted to slots and that slot goes on, slot, and that slot dimension becomes and these slits, all those small-small slits they become atomic, of the range of atomic dimension and then there you have very good surface matching on the fracture surface. Let us say this is the fracture surface and then you have a very good surface matching which is the characteristics of stress corrosion cracking.

Now this is about these are the - there are three main mechanisms by which you can have SCC cracking where the dissolution would control the initiation as well as the growth. Now we have another mechanism which is a broad mechanism that is called cleavage controlled mechanism. You have cleavage control mechanism. In that cleavage control mechanism you have several subsections. Cleavage control mechanism it says it has a difference subsections. It could be absorption, adsorption induced, cleavage, localized plasticity. Absorption, induced, cleavage, localized plasticity. It could be atomic. It could be tarnish rupture mechanism, and then it could be film induced mechanism. Film induced cleavage mechanism, or it could be atomic surface mobility mechanism, atomic surface mobility and there are many varieties. Let us consider on those four varieties. So in case of adsorption, induced, cleavage, localized plasticity there are many species. For example you have a crack like this and the atoms are arranged like this. These are the atomic arrangement in the material. Those atomic species for example this is my atomic species which is the product of corrosion in this zone, in the crack-tip zone that can enter into the lattice and that can lower the let's say this one is put the following, this one is placed inside in this two atoms of the lattice of the main atoms of the metal. So if this is falling in this so this can lead to sort of lowering of inter-atomic bond strength. Inter-atomic bond strength that can be decreased because of this atomic adsorption at this crack tip zone and that would lead to lowering of bond strength and there could be easy deformation and then material, this crack can go in.

Now this is absorption induced cleavage localized plasticity. In case of tarnish rupture mechanism see if we see the tarnish rupture mechanism, tarnish rupture let's say we have a passive film. We have a passive film like this. This is the passive film. Now this is under static tensile stress. Now this and this passive film is brittle in nature and due to this deformation or the tensile loading on this brittle plastic brittle passive film you can have a sharp crack. This is my sharp crack which is getting in into the material and once it reaches to this surface. So it is experiencing a tough or ductile matrix and then there would be crack tip blunting. So what happens so next step, if you see the next step, the next step you have this crack which is like this because the blunting is happening. So again you have this is my passive film now,now until and unless once this fresh surface metal surface is exposed to the solution and here we have solution and because of the corrosion reaction you can have passive film formation again. So this is my reformation of my passive film and the crack stops. So that means here you have arrest marking. Here you have arrest marking. So crack is getting arrested.

Now the second step again, again this is under stress. So again you can have a small crack formation here and then crack is experiencing the tough matrix. So it is getting stopped here and due to that also you have the crack blunting and this metal surface is exposed to the solution again passive film forms. The next step would be again growth of this passive film again. So it would be further growing of this passive film. So then you have so again it will grow like this. So this would be little like this it will form. So like that way it will grow. So again here you have a crack arrest. So like that fill forms, film breaks, again fill forms like that. It will go on. This is basically the film rupture model and cyclic growth as well as fracture of film. That is actually this is fracture of film and then again growth and then stop and then again this process. So like that it will go on. So this is tarnish rupture model.

Now the point is this model you can see that this transgranular would be the nature of fracture surface because this crack is not growing into the middle – into the tough matrix rather it is only the crack is forming in the film. So the predominant nature of fracture surface would be transgranular. So in order to explain the inter-granularity through this mechanism what happens if you have – these are the grain boundaries. Now here you have passive film. Passive film. Now this is under tension. So now this grain boundary, the tarnishing action or the oxidation or film formation because the grain boundary zone is highly diffusive zone because of selective precipitation or selective segregation along the grain boundary. This zone will get tarnishing. Tarnishing would happen in this zone. So crack is forming like this and then it is getting stopped. Again this will grow like this so like this it would happen. So if we put it in a different color so the crack is growing like this. Here it is stopped. Again it grows like this. Here it is stopped and this film formation would be preferentially along the grain boundary. So that way we can explain the inter-granularity of fracture intergranular fracture so this is the modified tarnish rupture model. Then you have film induced cleavage mechanism. Film induced cleavage mechanism. This is basically, for example, if you have this is my surface where the crack has moved like this. Now here we have a dissolution and that corrosion reaction lead to formation of a passive film. It's almost similar like tarnish rupture but the salient difference in this case is the film is forming at the crack-tip because the crack-tip zone that metal is exposed to the solution and the corrosion reaction leads to the passive film formation and this is under tension. So there would be a sharp crack formation and that crack can also get into the adjacent metal surface, metal section, a metal volume and there would be a little extra growth of this brittle crack in the metal surface, in the metal volume before it's getting stopped because of the tough matrix and there will be crack tip blunting because of the local deformation. So then the growth is basically here. The fracture surfaces appear – the fracture is happening in the film and that sharp nature of the film it can also get into the adjacent volume of the metal and then brittle crack propagates little bit in the metal and here it stopped again. So then again here we have little extra growth and then this crack is growing like this and again you have passive film formation. Then again this crack is propagating and then again it goes to adjust in metallic volume. So like that it moves on, and there you have crack arrest mark. This zone, this is another crack arrest and if you would like to see this way, let's say this is my semicircular crack. Now this is one crack and this crack is moving this surface again. It will stop like this. So these are basically the crack arrest marks. So this is film induced cleavage mechanism and this mechanism can explain the SCC crack in copper zinc system or copper aluminum system where this copper zinc you have dezincified layer which is the porous nature, micropore forms at that zone. This is the surface of the metal surface which is let us say this zone you have dezincification. So you have small, small pores here and those pores act as say stress raiser and through that the crack can propagate inside the material by breaking the film surface. So this mechanism can explain the brittleness. It can explain crack arrest. Crack arrest marking or cleavage like facet it can explain and also it can explain discontinuous nature of crack growth. So this is film induced cleavage mechanism.

Then you have one more mechanism that is atomic surface mobility and here what happens. This is let's say this part atomic surface mobility. Here we have let's say this is the crack and these are all the atomic planes and now there could be surface diffusion of atoms. Surface diffusion of atoms from there these are the atoms. These surface diffusion of these atoms can diffuse away from this crack tip and the crack can grow inside and here the surface cell diffusion will the rate at which the surface cell diffusion is happening that will decide the crack growth rate and here the corrosion phenomena or the environment solution, the effect of solution would be it's basically the changes the diffusivity of those surface atoms and it is sometime associated with the low melting surface compounds. This atomic surface mobility it's related to low melting surface compounds and one example is carbon steel for example the carbon steel it cracks in the presence of nitrate solution and that is due to the low melting surface compound formation. So these are the in broad cleavage control mechanism.

Now we can check some of the other characteristics of stress corrosion cracking. Some facts which are very important to know. The one is -- so important facts. One is there would be stress effect. So depending on that stress at which there should not be any SCC for the particular system that would be decided by the solution. Then you have the metal or alloy nature. Also temperature, pH all can affect this stress, amount of stress that is needed to avoid that that is the minimum stress where the stress corrosion cracking phenomena cannot be observed in that particular metals, metal or alloy.

Now let's say if we plot stress on the y-axis and here we plot time to failure, the time taken, the total time taken let's say we have put a stress in a particular component and then that is exposed to a particular solution and then total time to failure, we always term it as TF, that we try to measure and say the graph becomes like this. So that means this is the minimum stress level. This is minimum stress level below which you don't experience any SCC for that particular metal or alloy in that particular solution at a particular temperature and pH values. So this is the stress effect.

Now you have, second you have the corrosion product. Corrosion product they are forming due to the reaction with the environment and that corrosion products sometime leads to a very high compressor for example you have a crack and here you have the corrosion products. Here you have the corrosion products, and that corrosion products sometimes push this crack like this. So that could lead to further extra – that would enhance the SCC so because this corrosion product let's say this is the corrosion product and if the volume of the corrosion product is more than the – is more than the particle or the metal which is getting reacted with the solution and forming that corrosion product then that would push this crack tip, the two parts of the crack tip and there could be extra growth or the enhancement of SCC. Then you have, now you see that the time to failure, this time to failure is a very important parameter to judge the SCC ability or SCC tendency of that particular metal or alloy.

Now this time to failure if you would like to see the importance of the time to failure now if you see this let us say this is my crack tip and this is my total object. Now we have this one under tension. Now gradually the crack tip is, crack surface is growing inside the material and now if this is a constant load now gradually the remaining section we have increase in stress and as it grows like this finally you have a all ligament, this ligament where we have that ligament will experience excessive stress which could be more than UTS which is upper tensile strength limit of that particular metal and once it reaches to UTS, there could be normal mechanical failure. Okay. So that means until and unless we check the total time to failure, we would not be able to, for example, up to this the metal has gone and then we stop the experiment, will not be able to judge whether the material would have a very good SCC resistance or whether it has a poor SCC tendency. So that way we need to understand the total time to failure. So for that if we plot a graph let's say I would like to plot growth rate of crack, SCC crack with time to failure initially if you see that initially the growth rate gradually increases and the slope is very small and when it reaches to this level where the UTS value increases, the stress value which is being experienced by this portion which is more than the UTS then the rapid growth rate would occur.

Now same thing if we would land here there with the material fractures. Okay. This is the fracture point. Now same thing if we would like to see the extension with time to failure, same thing initially you don't see much change in the extension. Now once it reaches to this level there will be rapid extension of the material and here it will fail. So the total time this time needs to be checked in order to find out the SCC susceptibility of the material. So that means if a particular metal when it is exposed to a particular solution that time this is TF for metal M or M1 and then another metal M2 which is being exposed to the same solution I would like to see the and the same stress level so that time if the TF M2 if it is greater than this so this M1 has better resistance to SCC. So this time to failure is important parameter in order to judge SCC tendency of a particular metal or alloy when it is exposed to a particular solution.

Then of course there would be environment factors and environment factors which are to be considered while explaining or while judging the SCC character of a particular metal and object. So fourth one is environment factor. Environment factor for example temperature, pH, composition, oxygen content; all of this can affect the SCC character of a particular metal or alloy. Let's say 304 stainless steel if we have oxygen then in NaCl we experience SCC so there would be SCC but if we don't have oxygen then in NaCl solution no SCC. So that means the environment would also affect the SCC character of a particular material or alloy.

Now let us come to the prevention mechanism or control. There are; one is stress if it can be lowered or if it can be decreased on the component then if we don't decrease the stress, the stress decrease means you can get rid of residual stress. You can get rid of residual stress by low-temperature annealing or if you don't want to decrease the stress the actual load component residual stress needs to be removed by low-temperature annealing but if there is no residual stress still you would like to prevent SCC and you would not like to decrease the design stress or the actual design stress then what you can do we can for example this is the cross section you are thinking of for a particular your application. Now in order to linger this SCC you can increase the cross-section this much so it can control the SCC so that means thickening is one effect, one criteria or you can decrease the stress. So you can decrease the load actually. So then you can also control or prevent SCC. Then eliminating critical environmental species. Eliminating species for example in case of 304 stainless steel we can get rid of oxygen by suitable deaeration technique and then we can control or prevent SCC. Now third one we can change the alloy and change alloy for example in this case we can determine what is the SCC character on the basis of time to failure at a particular load level or strength – at a particular stress level and then we can decide which alloy is to be used. Then we can have cathodic protection. Since cathodic protection can protect the material from SCC and that's what we our SCC is electrochemical in nature. Then we can also add inhibitors which will take care of those corrosive species which lead to corrosion. So inhibitor can decrease the corrosion, SCC tendency or improve the SCC resistance of a particular metal or alloy when it is exposed to a particular solution.

So these are the prevention mechanism or prevention ways or routes. Now let us these are about the SCC control. This is basically the SCC control. The stress corrosion cracking control. Now coming to the second level of corrosion cracking or second variety of corrosion cracking not the stress corrosion, since we have seen earlier that corrosion cracking they can be divided into three categories. One is stress corrosion cracking. One is hydrogen embrittlement or hydrogen related cracking phenomena and then you have corrosion fatigue. Let us move to hydrogen related cracking. You can have in that section you can have hydrogen embrittlement. Then you can have the decohesion. Then hydrogen induced plasticity. Then fourth one there could be hydrogen blistering. So there could be around four different ways of hydrogen related cracking. There could be one more thing that is decarburization but that is not under hydrogen related embrittlement effect. So this is the hydrogen cracking, hydrogen related cracking phenomena. These four are there. So we see there are four major categories or four major sections by which hydrogen related cracking can happen in a material. Let us come to first stage which is a hydrogen embrittlement. Hydrogen embrittlement in this process if a material let's say we have a crack like this and this crack is under tension and if there is in the crack-tip zone in this zone you have atomic hydrogen formation and if your material contents titanium or zirconium those are the titanium hydride forming elements. So this hydrogen can diffuse in and reacts with hydrogen and then they can form hydrides. They can form hydrides and these hydrides are brittle in nature. So that crack again advances and then again you have this hydrogen generation, again hydride forms and then again crack advances like this and like that way the cleavage fracture propagates inside the material. This is called hydrogen embrittlement and the source of this hydrogen is cathodic reaction which is H++e which is H this cathodic reaction where you form hydrogen. These hydrogen can diffuse in and form hydrides with hydride forming elements and make the crack-tip zone brittle and the crack can propagate through that brittle zone and again it experiences the tough matrix. There it is stopped again hydride forms. That way the crack propagates. The second stage is basically decohesion. Decohesion says that if hydrogen goes in the material then it reduces the inter-atomic bonds for example you have crack tip like this and there are atoms which are bonded like this. These are the atoms which are bonded like this. Hydrogen can get in and then it weakens this internal atomic bond strength and if it weakens the crack can propagate because at a lower stress value the crack growth can be possible and here actually it reduces the surface energy. So if you consider the fracture stress okay if there is a relation, Griffith relation where fracture stress is related to, this is my Griffith relation where this is my surface energy and C is basically the half of the crack length and E is elastic modulus of the particular material. Now this atomic hydrogen goes there inside the bond and then it reduces this one, the surface energy reduces and once it reduces you see this one would also reduce so at a lower stress the fracture can happen. So this is called decohesion theory. Then you have hydrogen induced plasticity. hydrogen induced plasticity it says that at the crack-tip you have the crack-tip in this case hydrogen can decrease the resistance to – it decrease the resistance to dislocation movement, resistance to dislocation movement that can be reduced due to the hydrogen and then deformation can be easily possible. So the crack can – this zone can be deformed and then there the crack can propagate due to once it deforms the strain hardening can happen and then as but actually hydrogen reduces the dislocation movement so the strain hardening effect would be much less. So the crack can propagate easily. So this is hydrogen induced plasticity and if you come to the hydrogen blistering, let's say on a particular surface you have this reaction. This is my surface and over which hydrogen generation can be possible from hydrogen plus this reaction. Again here one hydrogen atom and another hydrogen atom and then instead of combining on the surface they can diffuse inside these atomic hydrogen and same thing would happen from this end also. These are basically diffusing in hydrogen atomic hydrogen and if let's say there is a small void inside the material the hydrogen can go there. Here it can go and in this case those two hydrogen can join each other and form hydrogen molecule and then gradually in this zone pressure increases and that pressure could be a few very high pressure which would be which is almost close to some 100 Pascals. So 100,000 atmospheres. So in this case the pressure could reach to around more than 100 atmosphere or something like that. So at that pressure this brittle fracture can propagate and there could be blistering effect on the surface. So this is called hydrogen blistering. So now we have four different ways of hydrogen induced cracking. Now this hydrogen induced cracking phenomena can be stopped if we can take care of those hydride forming elements or somehow we reduce the hydrogen formation or somehow if we can take -- if we can introduce inhibitors which will take care of this atomic hydrogen. So this way we can protect hydrogen embrittlement effect or hydrogen related plasticity and somehow if we can reduce this void formation inside the material this happens in case of rimmed steel. So if we can avoid this void formation the hydrogen blistering can be avoided. So these are some ways to protect material from hydrogen related cracking phenomena.

Then the last process by which corrosion cracking can happen. That is fatigue failure, corrosion fatigue. So corrosion fatigue is the final variation in corrosion cracking. So it can happen for example if a material, let's say on particular material which is exposed to a stress which is alternating in nature then you have compressive tensile component. This part is tensile component. This part is compressive and due to this alternate stress variation in the material. So the material can crack or fracture below yield stress and that time the material is called -- is said to be under fatigue failure, said to be gone under this and then gone for fatigue failure. So this if you would like to see the stress level and then you can see the number of cycles at which we have the fatigue crack formation of fatigue fracture. So we can for a particular steel let's say the steel it's like this, so that means this is my fatigue limit. So below this stress we can have any number of cycles without having any fatigue failure and for in case of non-ferrous you don't have any definite fatigue limit. So that time we decide some particular number of cycles for example if we decide some particular number of cycles 10 to the power 8 number of cycles so that would be the fatigue limit. So this is my fatigue limit. So that way we can decide what could be the fatigue strength of the particular material and if you would like to see the fatigue surface appearance you have a very smooth zone and then you have a very rough zone. This is rough and this part actually the actual and if you see there let us say this material this crack is growing via fatigue mode then up to certain limit the fatigue crack and propagate and after that you have a small ligament which is failing because which is failing due to the mechanical effect that means in this small ligament you have the stress which is more than the ultimate stress which can be withstood but the material by the material so the normal failure can happen and in this zone you have the smooth appearance and in this zone you have this rough appearance and this smooth appearance is due to the fact for example you have continuous load reversal or the stress reversal. So during this process with a tensile mode this is extending and during this process these are basically closing down so when it closes down that you have the pounding effect. The pounding effect during closing down process and due to that this surface becomes very smooth that means all the features which are forming, all the fins which are forming due to the crack formation those are getting smoothen out and so that means that surface becomes smooth but the rest of the surface where we have mechanical failure it will be rough in nature. So that's why the effective surface becomes like this.

Now when we have corrosion in addition to this alternate stress then the phenomena would be called corrosion fatigue. So this mechanical fatigue failure plus corrosion if we add that time we have fatigue corrosion. So the definition is basically and when you have this corrosion affect the fatigue corrosion, fatigue resistance of the material would reduce. So if you have the corrosion effect along with fatigue so the fatigue resistance would go down. Now during that process the surface this surface would always be rough. At the same time if we have corrosion together with the fatigue phenomena this smooth zone would not look a smooth surface rather you will have a corrosion debris or corrosion product on this material for example those are corrosion products. This corrosion products would form on this zone where you have the crack propagation via this fatigue action as well as the corrosion is happening so you have the corrosion deposit. So this is the fracture surface appearance if we have corrosion fatigue in corrosion fatigue.

Now what could be the mechanism? Mechanism generally when we come to see the corrosion fatigue in case of even in case of steel instead of having a well-defined fatigue limit we can have the nature in this case the nature, this case for example steel, steel we have this nature without the presence of corrosion and this is for non-ferrous metals and alloys where you have a smooth fatigue curve but in case of steel if there is corrosion then instead of having a smooth surface it will have a – instead of having a very defined well-defined fatigue limit we have a very smooth curve without having well-defined fatigue limit and mechanism it says that if we have, for example, on this zone this is my crack tip and if you have a pitting here this zone if we have pitting or even if you don't have crack let's say this is my surface and if we have a pit, this pit, this a small pit and this pit if you zoom it would look like a crack and due to this alternate stress reversal this pit would grow and then lead to fatigue failure. Pit growth by the this pit section will grow due to this alternate stress reversal or the fatigue action and then there could be corrosion fatigue.

So that means so from this we can understand that what could be the protection mechanism for fatigue failure. Definitely the material is one issue. We have to have a very good material which have inherent fatigue resistance and then of course, we have to make sure that there should not be any pit formation. If we don't have pit formation the fatigue failure due to corrosion, the corrosion fatigue failure tendency would be less. Now that means if we would like to avoid pitting then we have to take care of environment factor. Environment factors that means when we come to environment factors definitely oxygen content. Then temperature. Then pH solution. Concentration corrosive species concentration all the things are to be taken care of and also we have to see that there should not be any crevice formation. There should not be any the material should have inherent pitting resistance. So those can prevent the corrosion fatigue. So that means overall we see the stress corrosion cracking effect and this corrosion cracking effect can form due to three reasons; one is stress corrosion cracking. There could be hydrogen embrittlement or a hydrogen related cracking, and there could be corrosion fatigue. So these are and we have also discussed what are the factors for different corrosion cracking as well as the protection mechanism, and these are about the eight forms, this is the eighth last form of corrosion and so we have discussed all the eight forms of corrosion. Now we discuss two special types of corrosion that is liquid metal corrosion and microbial corrosion.

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