Fracture, Fatigue and Failure of Materials
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Lecture No – 28
Environment Assisted Fracture (Contd.)

Hello everyone. Here comes the 28th lecture of this course Fracture, Fatigue and Failure of Materials. And in this lecture also, we will be talking some more about the environment assisted fracture.

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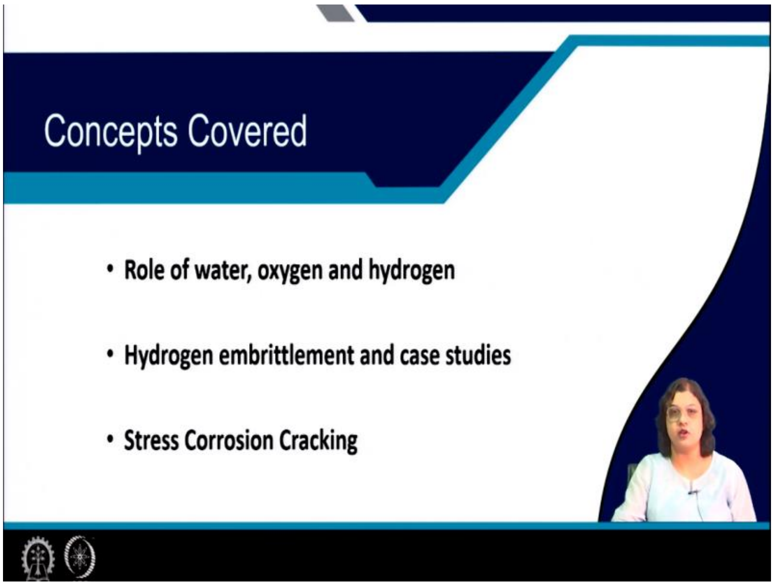

Concepts Covered

- Role of water, oxygen and hydrogen
- Hydrogen embrittlement and case studies
- Stress Corrosion Cracking

Particularly we will look into the effect of water, oxygen, hydrogen etcetera on the fracture behavior of materials and particularly we will look into the hydrogen embrittlments system once again in a little bit thorough nature with some more case studies and then we will proceed with the mechanism of stress corrosion cracking.

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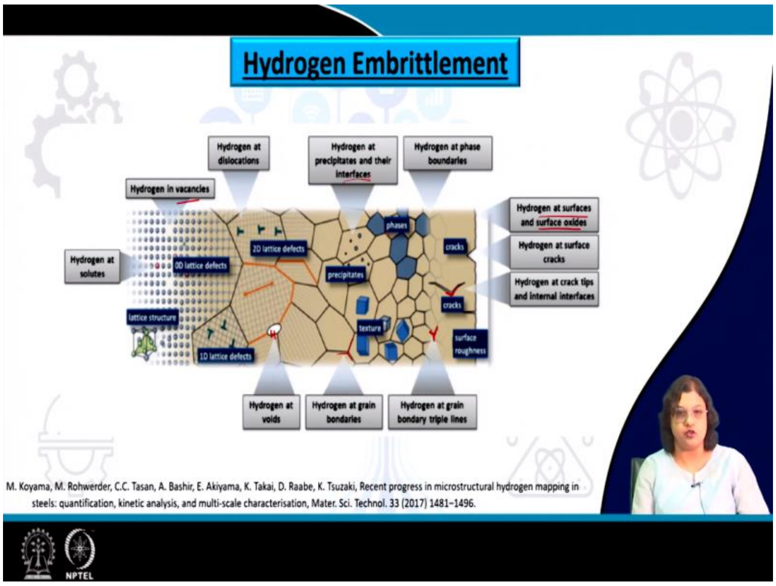

Hydrogen Embrittlement

Hydrogen at dislocations

Hydrogen at precipitates and their interfaces

Hydrogen at phase boundaries

Hydrogen in vacancies

Hydrogen at solutes

Hydrogen at surfaces and surface oxides

Hydrogen at surface cracks

Hydrogen at crack tips and internal interfaces

Hydrogen at voids

Hydrogen at grain bondaries

Hydrogen at grain bondary triple lines

M. Koyama, M. Rohwerder, C.C. Tasan, A. Bashir, E. Akiyama, K. Takai, D. Raabe, K. Tsuzaki, Recent progress in microstructural hydrogen mapping in steels: quantification, kinetic analysis, and multi-scale characterisation, Mater. Sci. Technol. 33 (2017) 1481–1496.

So, this is in brief what we have discussed in the last lecture about the presence of the hydrogen at the different places. So, let us look into this in little bit more details. So, what we can see here is the hydrogen, the presence of hydrogen could be either at the solutes or this could be at the different other places such as the zero-dimensional lattice defects or in the lattice structure itself.

It could be in the one-dimensional lattice defects or the two-dimensional lattice defects such as the grain boundaries and all. By one dimension, I mean the dislocations on which the hydrogen can get absorbed or get trapped. As you can see here the hydrogen can be present on the dislocation itself. Hydrogen could be also in the vacancies or in other voids for that matter.

Hydrogen can also be present at as I mentioned the void here or at the grain boundaries. So, these areas which are anyway higher at the energy level will be more prone to absorb the hydrogen and thereby create the internal stresses that will develop the crack and lead to the final failure. Particularly the triple point is the location which are more prone to absorb the hydrogen or accumulate the hydrogen.

Also, if there are some defects such as the cracks presence of cracks such places also because of the stress concentration are very much prone to absorb the hydrogen or accumulate the hydrogen and that will lead to the onset of the hydrogen embrittlement process as such, other than that hydrogen can also be present at the surfaces, as well as on the surface oxide. So, we have seen that in the case of the corrosion reaction to occur there will be the passive layer which forms typically the oxide layers are formed which also acts as a position that the hydrogen can be present. Other than the grain boundaries hydrogen can also be present at the phase boundaries or the inter phases. So, these are the locations in which also hydrogen can get stored.

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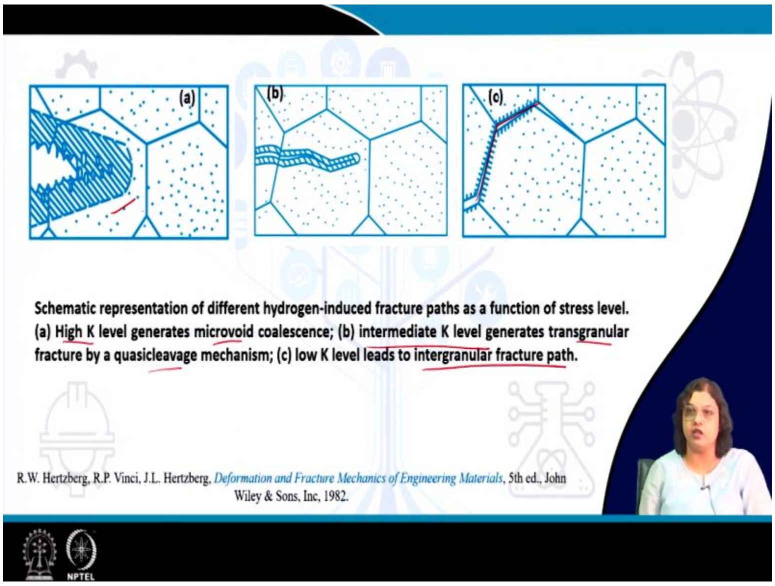

Schematic representation of different hydrogen-induced fracture paths as a function of stress level. (a) High K level generates microvoid coalescence; (b) intermediate K level generates transgranular fracture by a quasicleavage mechanism; (c) low K level leads to intergranular fracture path.

R.W. Hertzberg, R.P. Vinci, J.L. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 5th ed., John Wiley & Sons, Inc, 1982.

But wherever it is if we are changing the values of the stress intensity factor that can also change the mode of fracture as well. So, presence of the hydrogen while it generates the internal stresses and that will aggravate the situation of the cracking process if we are applying higher values of stress intensity factor that leads to early onset of the micro voids and then this micro voids with coalescence and that will lead to the progress of the crack as has been seen in this figure here.

On the other hand if we are applying intermediate K level so that means that the K value or the stress intensity factor value is not significantly high that also generates trans granular fracture, but in this case it should be in the quasicleavage mechanism. If we are however applying lower values of stress intensity factors that tends the hydrogen to pass through the grain boundaries because the grain boundaries are the weak part which are already in the high energy state and through which we are achieving the intergranular fracture path.

So, this is another indirect way of understanding how much of the K level or stress intensity factor level at the point of fracture in case we are dealing with the post fracture or the postmortem studies based on the Fractography. We can understand that based on the intergranular fracture or cleavage fracture we can understand the K level as well.

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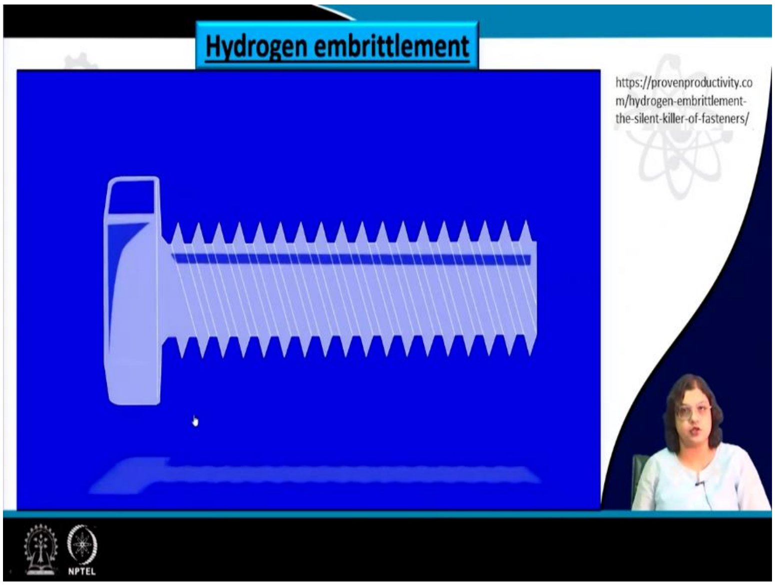

Hydrogen embrittlement

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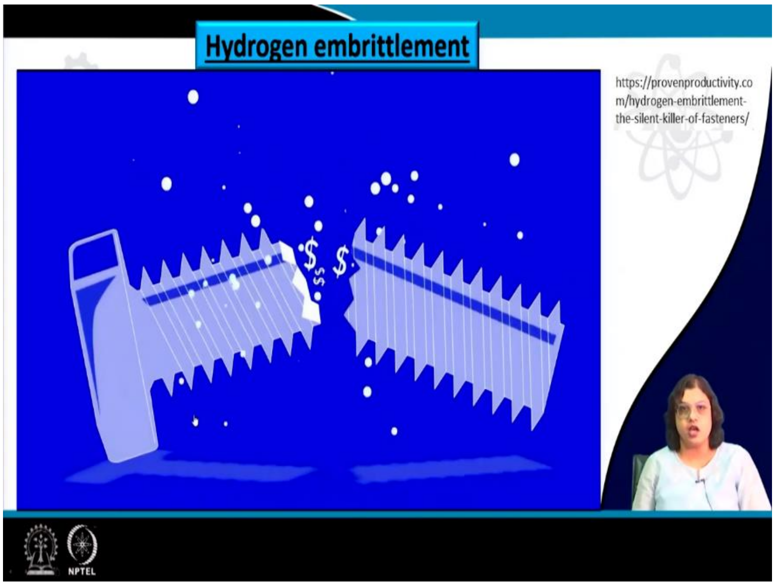

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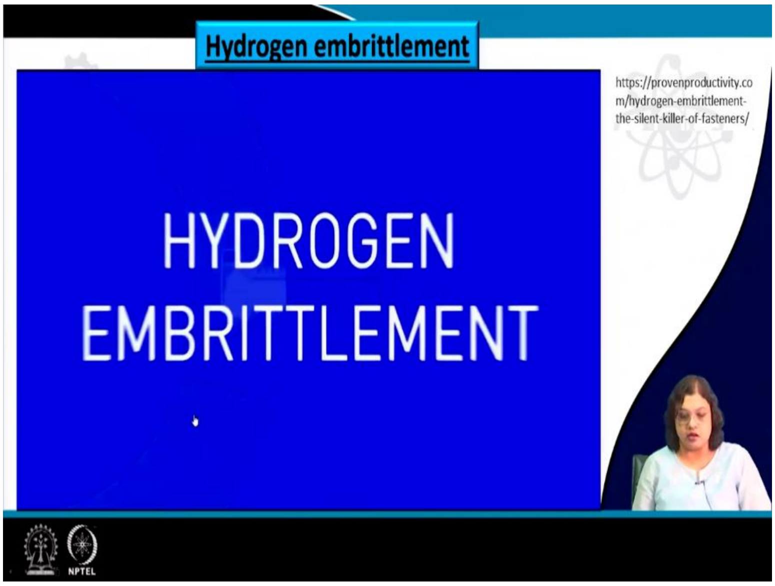

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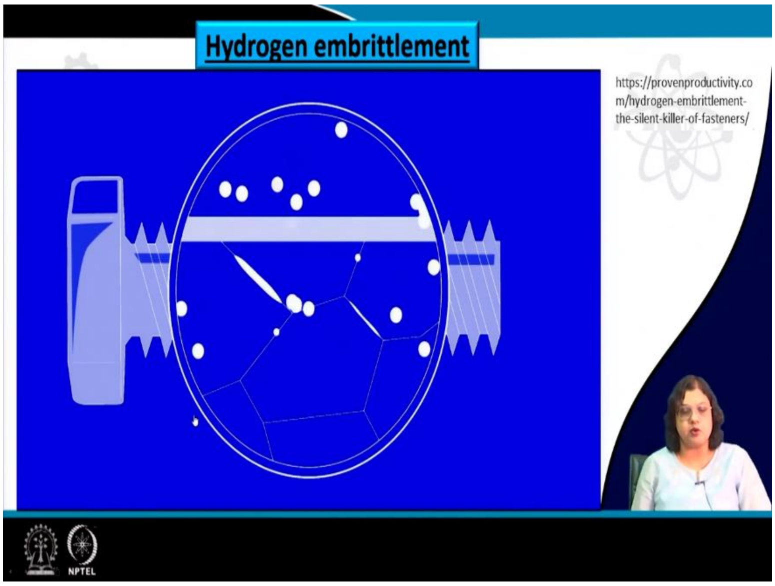
HYDROGEN
EMBRITTLEMENT



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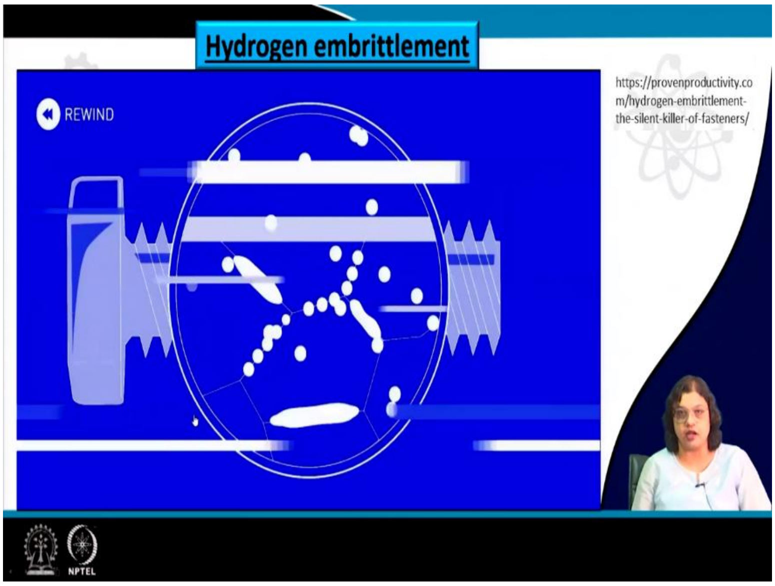

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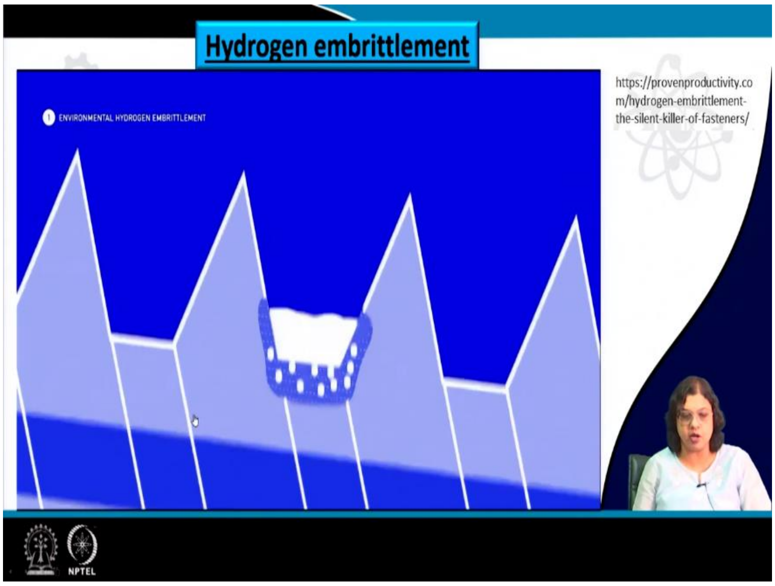

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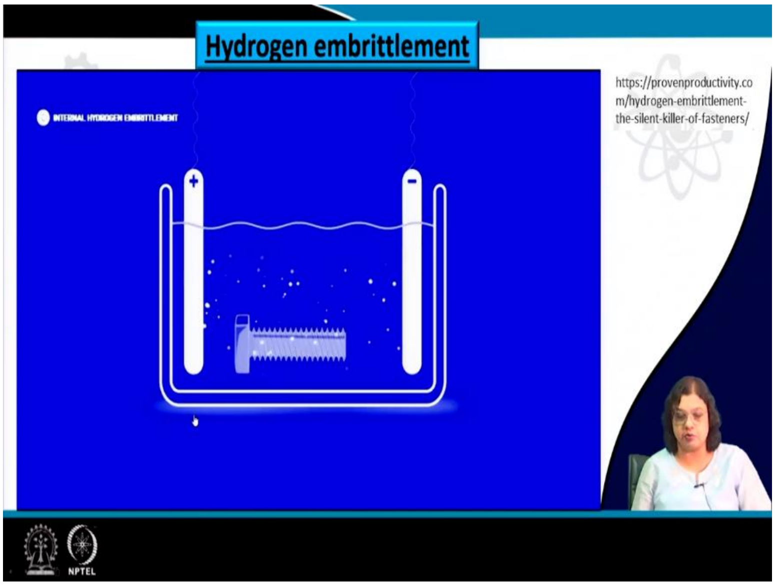

Hydrogen embrittlement

INTERNAL HYDROGEN EMBRITTLEMENT

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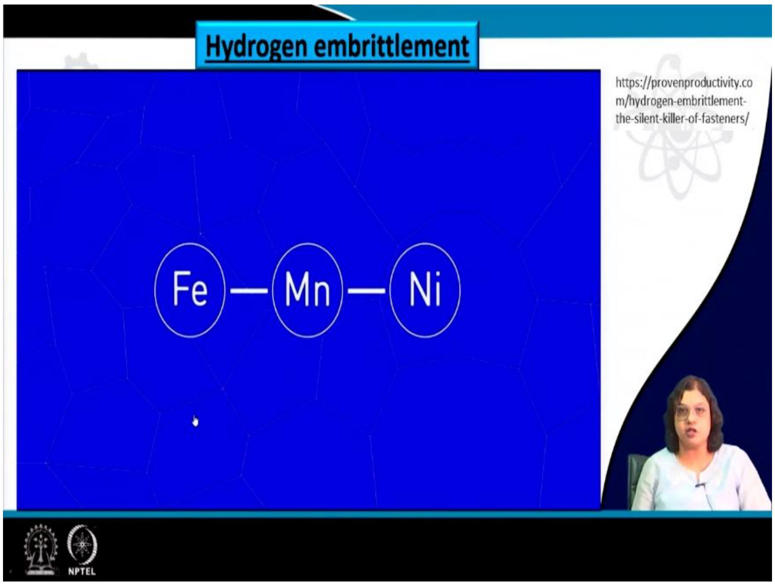

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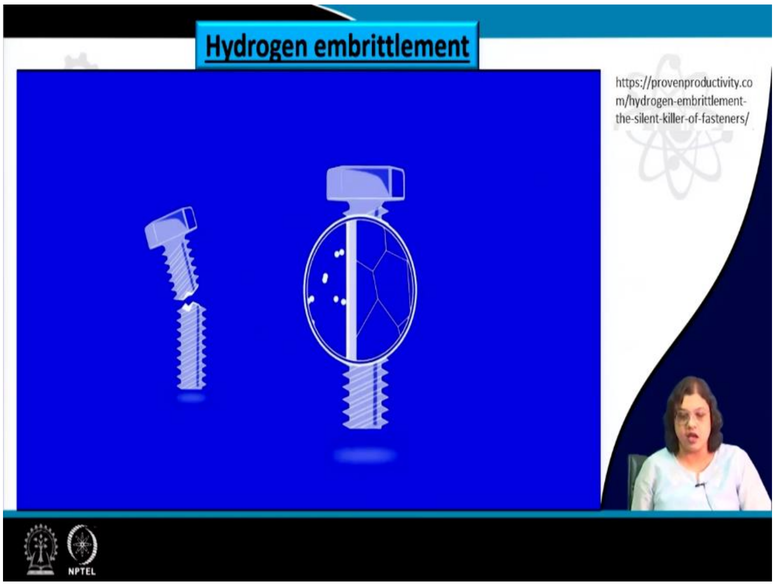

Hydrogen embrittlement

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So, this video here summarizes the hydrogen embrittlement process as has been seen for the case of screws. It often seen that it breaks down and that leads to significant expenses particularly this is a worse situation in case this happens during the service condition. So, because of the presence of hydrogen in the atmosphere or in the corrosive reaction or sometimes inside the system that leads to accumulation of hydrogen at the different locations as I have just shown and that leads to fracture of the entire component.

So, there are two different ways by which this can be used either this could be based on the presence of hydrogen in the environment through the corrosive reaction or it could be during the manufacturing process itself by which the hydrogen can enter there during the process of welding or electroplating as has been discussed already. This is applicable not only for plane carbon steel, but also for alloy steel or some other materials metallic systems as well in which hydrogen acts as a detrimental site.

So, particularly in presence of the stresses and tensile stresses this hydrogen embrittlement is more severe and that leads to failure in the cold condition so during the service condition which is one of the reason that hydrogen embrittlement has to be considered very severely. So, we can make some protective coating at the surface which will not allow the hydrogen to pass through the protective coating and enter into the lattice.

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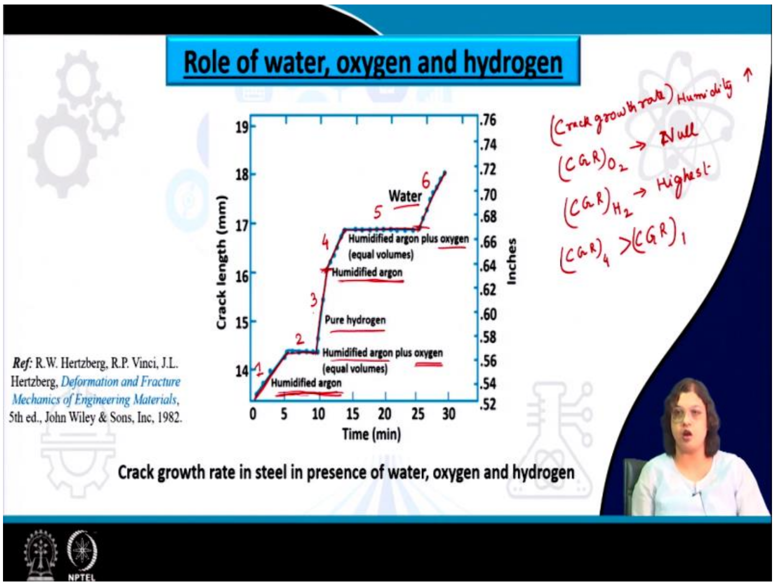

Role of water, oxygen and hydrogen

Ref: R.W. Hertzberg, R.P. Vinci, J.L. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 5th ed., John Wiley & Sons, Inc, 1982.

Crack growth rate in steel in presence of water, oxygen and hydrogen

(Crack growth rate) Humidity ↑

$(CGR)_{O_2} \rightarrow$ Null

$(CGR)_{H_2} \rightarrow$ Highest

$(CGR)_4 > (CGR)_1$

Now, this graph here very interestingly shows how the crack growth will behave or will occur with respect to time in different conditions. So, let us see how it behaves in presence of the humidified argon. So, argon anyway we are well aware that argon is a medium through which if there is an inert medium through which the crack or any kind of reaction is not supposed to happen.

But in case we are having the humidified one which means that there is the moisture that is present there. So, basically there is a presence of H_2O which could be the source of hydrogen that may embrittle the system and we can see that the crack growth rate or the slope of this curve is quite high for the case of the humidified argon, had it been just the inert atmosphere there would not have been any growth at all.

But what we are seeing here interestingly is that if we mix this humidified argon with equal volume of oxygen which means that we make it a 50-50 combination of humidified argon along with oxygen. The crack growth rate is getting completely arrested. Now, that is very interesting while at one case we are seeing the crack growth rate in presence of humidity for example is quite high.

The crack growth rate in presence of oxygen is actually 0. So, crack is getting completely arrested in presence of oxygen. This although looks surprising the actual fact is that this oxygen forms the oxide. So, this helps in forming the oxide and we have also seen earlier that in most cases for the metallic system this oxide acts as a protective or passive coating. So, that would not allow the corrosion reaction to proceed further.

And that will stop the crack length at least momentarily unless we have some other situation like enhancement of the temperature, enhancement in the stress the crack is getting arrested in presence of the oxygen. Now, in the third step; so this is step 1 in humidity, step 2 in oxygen and in the third step in presence of pure hydrogen. So, this is not moisture anymore this is just pure hydrogen.

And we can see that the crack growth rate is the highest. So, crack growth rate in presence of hydrogen is actually highest. So, obviously hydrogen seems like is having the most detrimental effect on the crack growth rate. So, it grows very, very faster in presence of the hydrogen and that is all because of embrittling mechanism that weakens the bond along with this internal pressure that leads to early growth of the crack or faster growth of the crack.

Once again if humidified argon is applied to it we see in step 4 that this also grows quite fast although not as fast as hydrogen. So, the growth rate has reduced to some extent in compared to the step 3, but if we are considering the condition for step 1 and step 4 both are same. So, both cases we are using humidified argon, but what we can see here is that the crack growth rate for step 4 is higher than the crack growth rate for step 1.

Now, this is particularly because of the reason that the crack has already grown up to this extent. So, while it was initially starting from let us say 13 or 12 millimeter it has now come to around 16 millimeters so it means that it has enhanced the length of the crack and we also know that the crack length is directly proportional to the stress intensity factor at the tip of the crack.

We have seen that K is function of $\sqrt{\pi a}$. So, that means that if a is increasing k is increasing and that means that with highest stress intensity factor of course the crack will grow at a faster rate. So, that is the reason that we are seeing the crack grows at a faster rate for step 4 in comparison to 1. But once again if we are putting the oxygen into the system for step 5 we are seeing that the crack growth rate has come down to 0 which means that the crack is getting completely arrested if we are using the oxygen once again due to the formation of the oxide layer.

If we are using the moisture or simply the water we can see that the crack growth rate is increasing once again this appears to be a little bit higher than step 1 particularly because of the crack length and because of the absence of argon so that is one effect as well as the enhanced length of the crack that is another effect that is why we see ultimately although this is only the schematic way water as well as the humidified argon shows more or less same crack growth rate.

But as I mentioned that there are the two factors acting together here one is the argon which is nothing, but the inert atmosphere which is not there in this case. On the other hand, we also have seen that the crack has grown to a few millimeter now when we are adding water so that also acts in a way of enhancing the crack growth rate which nullifies part of the absence of argon phase 1. So, that leads to more or less equivalent crack growth rate as that of step 4. So, such is particularly is the case when we are talking about the hydrogen embrittlement and how it affects the material.

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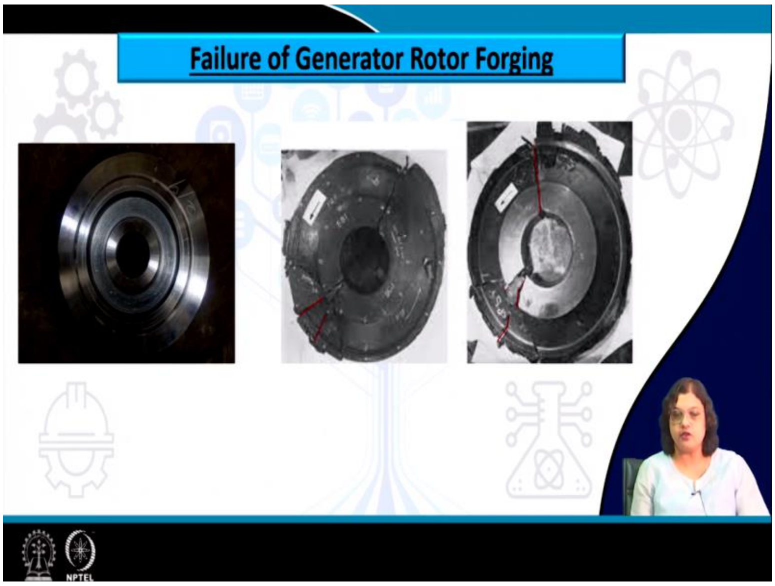

Failure of Generator Rotor Forging

And this is an example of how generator rotor which has been typically forged and because of the hydrogen embrittlement this just fails all of a sudden into the brittle pieces and you can see this fails in many such pieces. So, this signifies that this is the brittle mode of fracture we can see that failure has occurred at several locations. So, certainly this signifies that this is a brittle failure and hydrogen has been already entered into the system at several locations which lead to this final fracture and this is again an incident of cold cracking. Suddenly during the service itself after several years of work one fine morning it just fracture on its own. So, this is more or less what we have seen for the hydrogen embrittlement.

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Stress Corrosion Cracking

Requirements

Susceptible materials

Static stress

Aggressive /corrosive environment

And now let us move on the stress corrosion cracking. Now, stress corrosion cracking is another way by which material or system component can fracture at a lower values of stress intensity factor then what is applied and the particular requirement or particular factors that are required to have this materialize the stress concentration, stress corrosion cracking are the following.

We need a material which is susceptible to stress corrosion. Not all the material systems will undergo stress corrosion cracking only those material which is susceptible to the corrosion reaction can only go through stress corrosion cracking also along with that along with the material being susceptible we need a stress and amount of stress that is already existing during the service or in the process itself.

So, this stress is very important for the stress corrosion to materialize and thirdly and most importantly as the name suggest we do need a corrosive or aggressive medium. It is not that we need that, but these three conditions simultaneously ensures occurrence of stress corrosion cracking. If we have just susceptible material, but not aggressive environment that may not lead to any cracking at all.

On the other hand, if there are susceptible material as well as aggressive environment, but there is not enough amount of stress present there that may lead to some amount of corrosion, but that may not lead to the cracking and the fracture. So, we need all these three conditions to be acted simultaneously to materialize the stress corrosion cracking.

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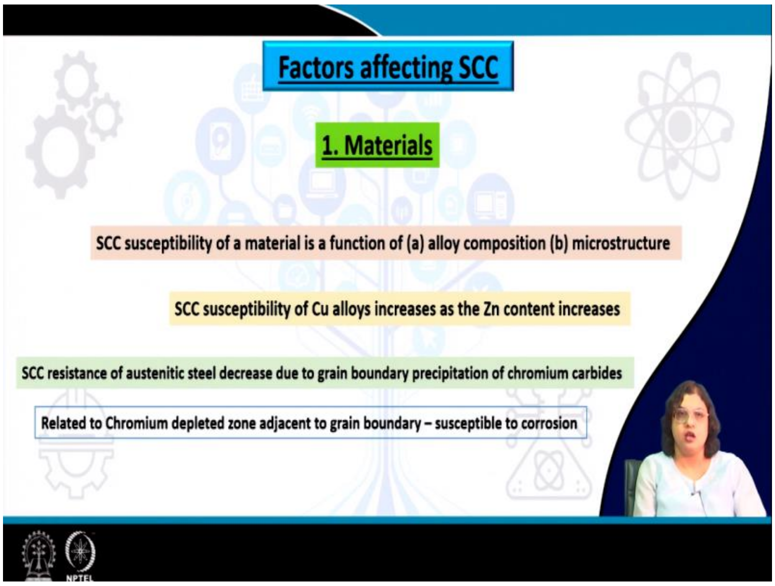

Factors affecting SCC

1. Materials

SCC susceptibility of a material is a function of (a) alloy composition (b) microstructure

SCC susceptibility of Cu alloys increases as the Zn content increases

SCC resistance of austenitic steel decrease due to grain boundary precipitation of chromium carbides

Related to Chromium depleted zone adjacent to grain boundary – susceptible to corrosion

The first one let us see the materials particularly the susceptibility of the material to stress corrosion cracking is a function of the composition. We are mostly talking about the metallic systems here. So, the alloy composition is very, very important and the microstructure. Microstructure anyway is dictating almost all the mechanical properties of material. So, both of this together will dictate that whether the stress corrosion will happen or not or even if it does how will be the severity of the corrosion reaction.

Now, some particular metallic system as well as the corrosive atmosphere combination of those or as well as two different metallic systems. The combination of two different metallic systems that undergo such kind of corrosive reactions needs to be known and if not that may lead to some severe damage during the service. So, it is know that SCC, the stress corrosion cracking susceptibility of copper alloy is particularly related to the zinc content.

If the zinc content is increasing that may make the copper more susceptible to undergo more prone to undergo stress corrosion cracking. On the other hand, for the case of austenitic steel stress corrosion cracking resistance that decrease due to the grain boundary, precipitation of chromium carbide. Now, chromium carbide if those are getting precipitated at the grain boundary means the immediate adjacent neighbor the vicinity of the grain boundary that gets depleted of chromium. Chromium is very well known for the corrosion resistance of steel.

Now, if that location adjacent to the grain boundary which is anyway at a high energy state and that gets depleted of chromium that makes the alloy or that makes the steel more prone to undergo stress corrosion cracking. So, that is what we should be careful of while considering steel for some particular application which have the possibilities to undergo stress corrosion cracking.

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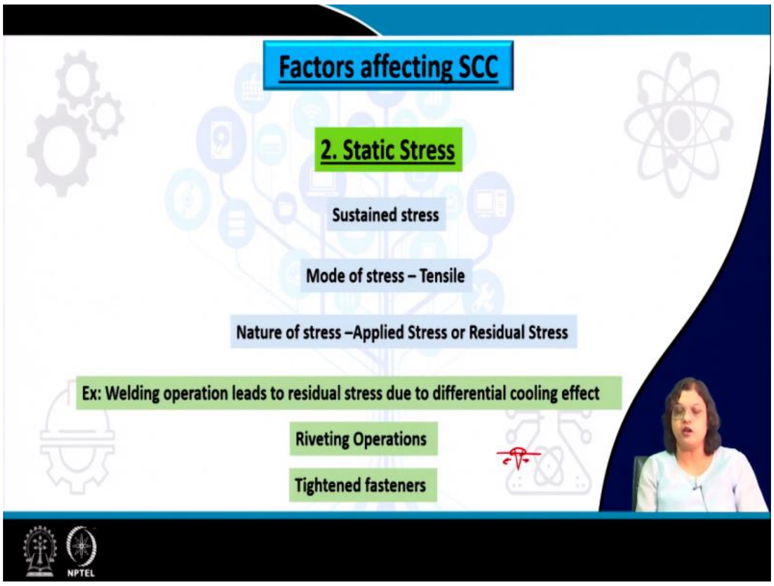

Factors affecting SCC

2. Static Stress

Sustained stress

Mode of stress – Tensile

Nature of stress –Applied Stress or Residual Stress

Ex: Welding operation leads to residual stress due to differential cooling effect

Riveting Operations

Tightened fasteners

The second factor is the static stress. The stress need not be cyclic it may also happen with cyclic loading or fatigue loading, but even if this is just a static stress which means that there is a continuous application of a particular amount of stress, particular magnitude of stress that is also sufficient for stress corrosion cracking to occur. So, this stress has to be sustained and the mode of the stress that actually will lead to stress corrosion cracking is tensile.

So, had it been a compressive stress once again we have seen that compressive stress is not so detrimental for the crack because the crack tend to close under compressive loading. So, tensile stress particularly is very much makes the material susceptible to undergo stress corrosion cracking. The nature of the stress, how we are applying the stress that is not important.

We can apply the stress or the stress could be present in the system already as a residual stress. So, both ways this will act in a same manner that this will let the corrosion reaction to occur and whatever cracks or defects are there that will initiate growing or grow at a faster rate because of the presence of this either applied or residual stresses. Now, some of the example that leads to stress corrosion cracking is during the manufacturing process itself that, for example, the welding operation that leads to the residual stresses due to the differential cooling effect.

The surface cools at a faster rate and the internal sections particularly the heat affected zone that will have a different cooling rate that will develop different micro structure that may also behave differently in the corrosive atmosphere and that will have a non-uniformity in the behavior most importantly and that can lead to the initiation of the crack growth of any kind of anomaly is there in the microstructure or in the stress distribution as such.

Riveting operation is very, very important particularly when we are punching the rivet sometimes the crack do generate and when we are doing this riveting thing itself and we are punching this rivet that also leads to generation of internal stresses. If the crack is forming that is a kind of releasing the stresses those cracks particularly under cyclic loading can lead to fracture.

But even if the cracks are not formed because of the riveting operation as we can see that if there is a surface and we are putting a rivet on top of this while doing that operation, while punching it the residual stress that is being generated particularly at the surface that can also lead to early onset of the crack and is reactive to the corrosive atmosphere provided such kind of atmosphere is available during the service.

Fastener which are being tightened of course once again we are performing these tightening operations and in particularly if we are doing this at a comparatively higher temperature that can lead to some changes even in the microstructure also and as we can understand during the tightening operation itself some internal stresses will be stored there which will act or which will aggravate the situation particularly in presence of a corrosive atmosphere. The corrosion reaction will take place at a faster pace and that will lead to earlier onset of stress corrosion cracking.

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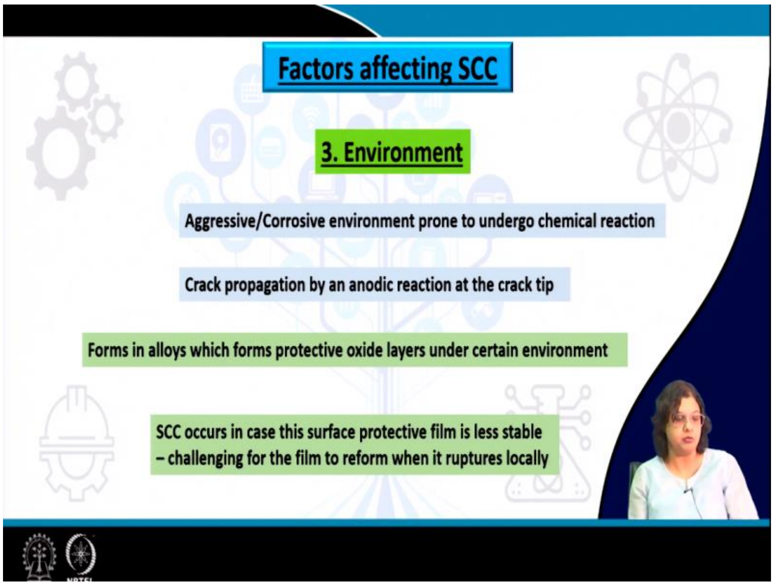

Factors affecting SCC

3. Environment

Aggressive/Corrosive environment prone to undergo chemical reaction

Crack propagation by an anodic reaction at the crack tip

Forms in alloys which forms protective oxide layers under certain environment

SCC occurs in case this surface protective film is less stable – challenging for the film to reform when it ruptures locally

Environment is certainly a very important one and once again we need to understand the different atmosphere or the material system, the combination of these two which will lead to the stress corrosion cracking. So, corrosive environment is prone to undergo the chemical reaction and the crack propagation will occur as an anodic reaction at the crack tip as we have already seen how the entire component behaves as an electrolytic cell with the presence of anode at the crack tip and the cathode at the weight of the crack which is covered or which is surrounded with the passive zone as well as the corrosive medium as a electrolyte.

This entire reaction will keep on occurring in presence of the environment and in presence of this tensile stress as well. So, this is particularly this environment is particularly important if the material is susceptible to undergo the chemical reaction. So, in cases where the material undergoes corrosion and then it forms a protective oxide layer that is actually although it sounds beneficial affected forming this protective oxide layer does save it from further corrosion to occur that is what happens regularly.

But if we are applying the stress to it then something else is going to happen which we will just discuss in a minute, but what is important and what I want to clarify here is that the presence of all these three factors is very, very vital then only the stress corrosion cracking will occur. As I mentioned this corrosive layer or the protective layer is beneficial to restrict the corrosion, but in case this protective film is not stable enough.

Then there will be a challenge for the film to reform in case it ruptures locally because of the presence of the stress a film which is not stable enough will rupture and once it does it again has to reform then only it can continue helping in arresting the corrosion reaction. If not, then the corrosive medium will percolate through this ruptured film and that will lead to further corrosion even in the interior of the component.

So, that is very, very important to ensure that if we cannot control or if we need to apply a material in the stress application which we know that there will be some amount of stress we should avoid the aggressive medium to be present there and vice versa. If we know that some component or some material will be used for corrosive applications then we have to be careful that there should not be any kind of applied or residual stresses present in the material. So, let us look into what actually is happening, what is the exact mechanism for the stress corrosion cracking.

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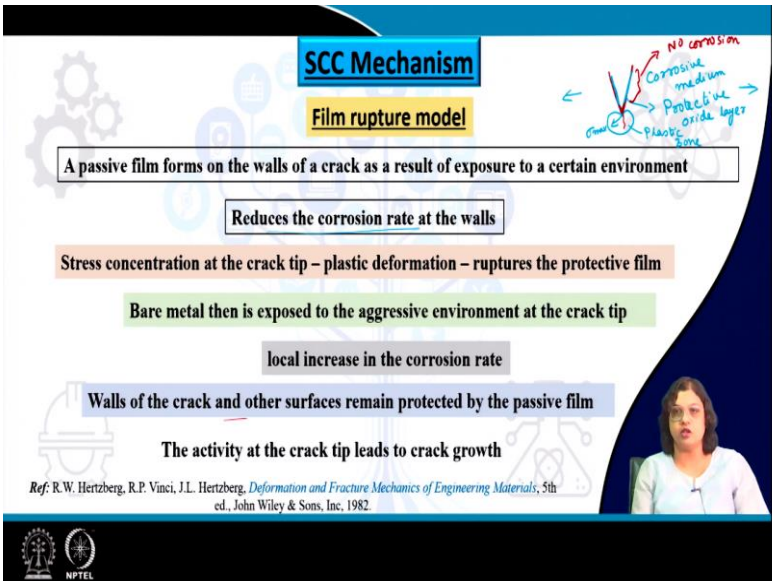

SCC Mechanism

Film rupture model

A passive film forms on the walls of a crack as a result of exposure to a certain environment

Reduces the corrosion rate at the walls

Stress concentration at the crack tip – plastic deformation – ruptures the protective film

Bare metal then is exposed to the aggressive environment at the crack tip

local increase in the corrosion rate

Walls of the crack and other surfaces remain protected by the passive film

The activity at the crack tip leads to crack growth

Ref: R.W. Hertzberg, R.P. Vinci, J.L. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 5th ed., John Wiley & Sons, Inc, 1982.

And what typically happens is the passive film forms on the wall of the crack as we have seen if there is a crack here. The passive oxide forms at the crack surfaces when this is so this is the corrosive medium and this is the crack. So, we have a protective or passive oxide layer this could be just the product layer and that prevents the crack or the material from further corrosion to occur that reduces the corrosion rate at the walls that is fair enough.

But the problem is that when we are applying the stresses and that to the tensile stresses. Tensile stresses on the crack means that this is a kind of crack opening mode the most detrimental one. So, in presence of this the film is going to rupture even if that is not the case or the applied stress is not that severe we already know that there is a stress concentration that happens here.

And we have also seen that how it forms the plastic zone ahead of the crack tip. Now plastic zone is a permanent deformation. So, once the plastic zone form it means that the passive layer which is form particularly at the tip is getting ruptured. So, that means the nascent crack surface is again coming in direct contact with the corrosive medium. So, that means that there are further chances for the corrosion reaction to occur.

And most importantly this nascent surface is now very much prone to proceed further that increases the locally the corrosion rate and in turn the crack is expected to proceed that means the growth of the crack will occur and it will happen at a faster rate. The walls of the crack on the other hand are still being protected with this corrosive layer and there will be no corrosion reaction at the wall of this crack, but at this part here there will be no corrosion. But the tip of the crack which is at its highest stress level or the maximize stress level that will lead to the film rupture and that will lead the crack to proceed at a faster rate.

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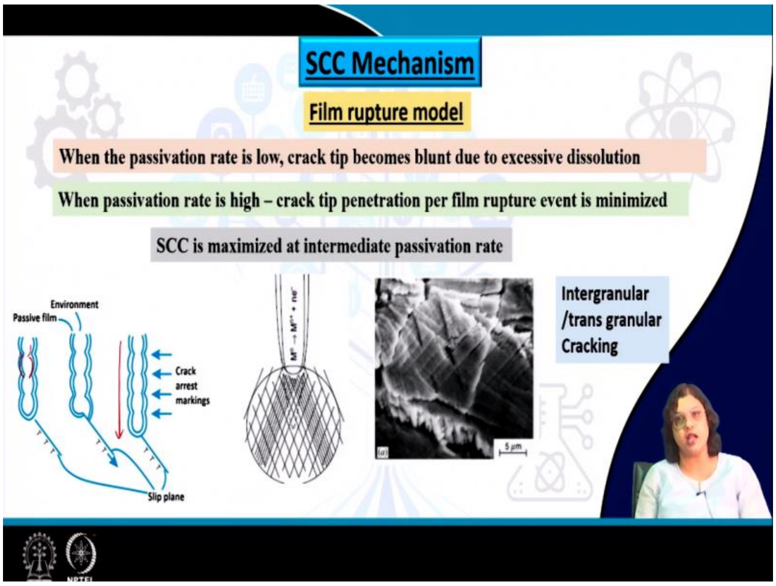

SCC Mechanism

Film rupture model

When the passivation rate is low, crack tip becomes blunt due to excessive dissolution

When passivation rate is high – crack tip penetration per film rupture event is minimized

SCC is maximized at intermediate passivation rate

Intergranular /trans granular Cracking

So, typically this is also related to the passivation rate the growth of the crack. When the passivation rate is low crack tip becomes blunt due to excessive dissolution, the corrosion reaction is happening and that leads to dissolute the material and that makes the crack tip blunt. Now, if the crack tip is getting blunt obviously the stress concentration factor reduces there and that means that the amount of plastic zone or the ability to plastic deformation also reduces.

And that means that the film may not get ruptured or even if it does it may not be that detrimental. On the other hand, when the passivation rate is high then the crack tip penetration per film rupture event is minimized. So, it is happening at a very faster rate so that means that there is not enough time for the film rupture to occur or to cope up with that rate particularly stress corrosion cracking is maximized at the intermediate passivation rate.

So, if the passivation rate is very, very high that is also not so detrimental. If the passive rate is low of course that is not so detrimental, but in the intermediate rate only the stress corrosion cracking is maximum. So, if we cannot control any of like the presence of the corrosive medium or the application of stress we can make sure that the passivation rate should not be very, very high or we have to use a particular material which may passivate at a moderate rate which will not lead to slower rate to make it less prone to stress corrosion cracking.

So, this is just the example of how the stress the film rupture model works. So, as I mentioned that this is a kind of discontinuous growth of the crack or in step wise the crack growth. So, initially the crack grows up to this part and then the film ruptures and there is a arrest in the crack growth rate for some moment, but then it regains again and it grows further and like that the entire length of the crack is increasing if we are applying this for a sufficient amount of time.

So, here also time is very important factor that we need to keep in mind and based on that the stress corrosion cracking can be delayed or can be advance and we need to utilize that for the service condition. This on the other hand shows the example when the crack growth rate is continuous like there is no such filming or there is no such way by which the crack growth is being interrupted by formation of the passive film.

If that is not there if the passive film is not forming at all then of course the corrosive medium that will be very aggressive for the corrosion reaction to occur and that means that the crack tip will get sharper and sharper because it acts as the anode and that leads to higher and highest concentration factor there and it will grow at a very faster rate. This is the fracture surface and particularly we can get both trans granular or intergranular kind of cracking in case of the stress corrosion cracking overall.

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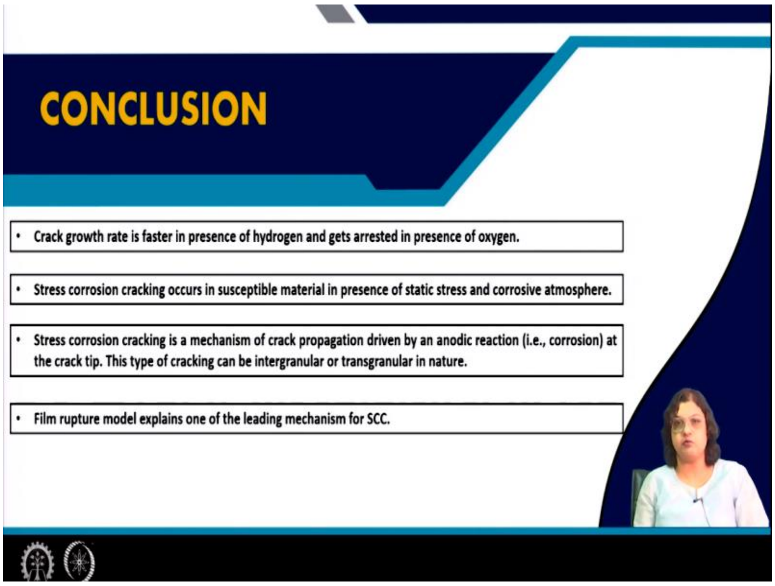

CONCLUSION

- Crack growth rate is faster in presence of hydrogen and gets arrested in presence of oxygen.
- Stress corrosion cracking occurs in susceptible material in presence of static stress and corrosive atmosphere.
- Stress corrosion cracking is a mechanism of crack propagation driven by an anodic reaction (i.e., corrosion) at the crack tip. This type of cracking can be intergranular or transgranular in nature.
- Film rupture model explains one of the leading mechanism for SCC.

So, coming to the conclusion for this part of the lecture what we have seen is the crack growth rate is faster in presence of hydrogen and it gets completely arrested while there is oxygen. Stress corrosion cracking occurs in a material which is susceptible to undergo corrosion in presence of static stress and the corrosive atmosphere. So, all these three factors the corrosive atmosphere, static stress as well as the material which is susceptible to undergo corrosion reaction.

All these factors need to act simultaneously for the stress corrosion cracking to materialize. Stress corrosion cracking is a mechanism of crack propagation that is driven by the anodic reaction as we have seen in the corrosion reaction it behaves like an electrolytic cell and the crack tip forms the anode and this type of cracking can be either intergranular or transgranular in nature. One of the leading mechanism for stress corrosion cracking is the film rupture model which has been discussed.

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Following are the references that has been used for this lecture. Thank you very much.