

Corrosion Failures and Analysis
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Lecture - 42
Stress corrosion cracking: Corrosion fatigue and protection methods

Let us start lecture 42 for the series Corrosion Failures and Analysis. And today, it will be the last lecture in this particular series. And we have been talking about stress corrosion cracking and we talked about different characters of stress corrosion cracking as well as mechanism.

While doing so, we saw that when stress corrosion happens that time, we also have some sort of foreign species. In this case, the foreign species is hydrogen and that hydrogen assisted cracking is also possible. And this hydrogen assisted cracking is actually categorized as a separate section, which is called hydrogen assisted cracking or hydrogen cracking.

So, there we talked about a couple of failures failure routes like hydrogen assisted cracking, which is which involves decohesion of atomic bonds. Then, we have hydrogen embrittlement which relates to hydrogen hydride forming elements and those are brittle phase and that is what the crack propagates through that hydride forming elements before it gets arrested by the tough matrix or the ductile matrix.

Then we have hydrogen assisted local plasticity which does not fall under embrittlement, but what happen the hydrogen diffuses in and actually helps in dislocation motion or prevents dislocation. It actually avoids dislocation movement not avoid its basically helps in dislocation movement or avoids obstacles for dislocation movement. So, that is why the dislocation that dislocation motion becomes easy and local deformation happens.

And if local deformation happens that plastic flow would lead to a local dissolution, as well as the crack can propagate through, because of the local dissolution and consequence of hydrogen diffusion and local plasticity. And then finally, we talked about hydrogen blister ok. So, that blister though we consider it to be hydrogen related failure,

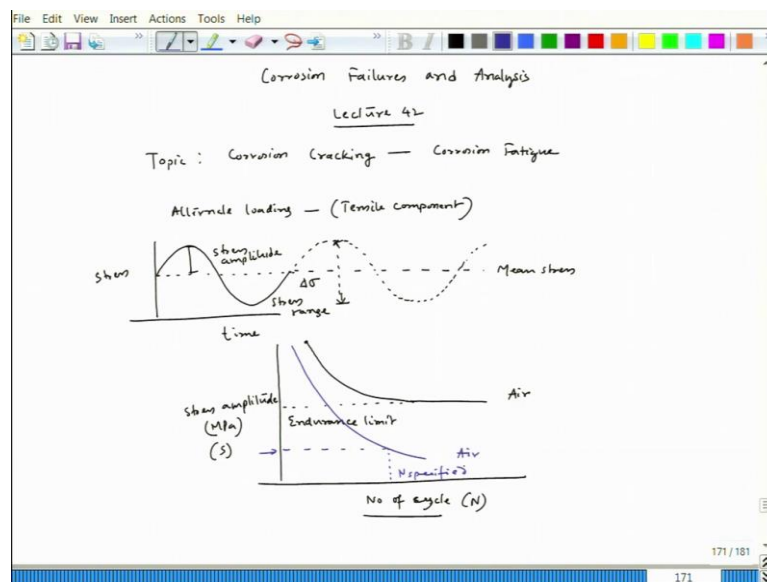
but that does not fall under stress corrosion cracking or hydrogen cracking, because it does not involve external loading or residual stress.

It actually happens due to combination of recombination of hydrogen atom within the voids in the material and that voids, because it requires a 1000's of atmospheres for equilibrium to set up between $2H$ equal to H_2 and that hydrogen pressure inside the small voids inside the material; it actually leads to a fish mouth kind of cracking.

Now, then we that is what the hydrogen embrittlement or hydrogen assisted cracking has been considered along with the mechanism study for SCC, because while hydrogen diffusion happens or hydrogen related cracking happens, tensile stress is also another factor. So, that is what we discuss that along with the mechanism of SCC.

Now, one more aspect of corrosion cracking that is corrosion fatigue. So, we will talk about corrosion fatigue and then finally, we will talk about different protection routes or processes what you can employ. So, that this stress related cracking can be mitigated or can be minimized.

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So, the course is corrosion failures and analysis and this is lecture 42 and topic is corrosion cracking. In that we will talk about corrosion fatigue. We know fatigue that if there is alternate loading and there is a tensile component in that alternate loading, the material fails quickly ok.

Now, if the loading is like this is time, this is stress and if this is the mean stress, then one can have loading like this ok. So, this continuous. So, I can extend this. It is going on like this, where this is stress amplitude this is the this gap the minimum and maximum this we can say $\Delta\sigma$ which is the stress range ok and it is having a frequency that alternate motion.

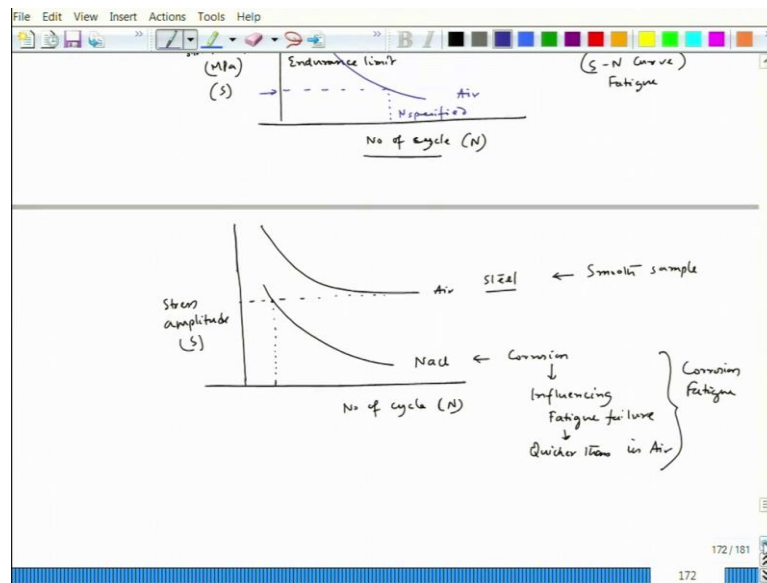
Now, if we actually expose a material a towards that alternate stress variation, the material will fail and we can actually plot stress amplitude which is nothing, but MPa against time sorry against number of cycle which is N. So, that is what this is S which is stress amplitude.

So, now this actually if you have a very high stress amplitude, it fails very quickly and if you have a low stress amplitude, it fails very it very quickly or at a very low cycle of loading. And if you have if you use a low stress amplitude, then definitely number of cycles till failure increases.

So, in case of steel, ferrous material it is happens like this. So, there is a kind of plateau region. So, this is called endurance limit. So, where below that stress amplitude, the material does not fail with amplitude with the number of cycles. Now, this happens in air ok. Now, in case of non-ferrous alloy so, this happens like this there is no definite stress amplitude. So, that case it happens like this. In that case, it keeps on decreasing.

So, that case what is done? We specify some level of number of cycle let us say, this is N specified and accordingly we choose the endurance limit. So, this is in this case this becomes my endurance limit. Now, if and this is also in air the testing has been done in air. Now, if the testing is done in corrosive solution, the situation changes.

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Let us say we have a steel and that is actually exposed to alternate loading you know corrosive solution. Let us say if it is air, it will have its usual endurance limit this is air. But in case of this is steel let us say, but if it is in corrosive, let us say NaCl solution. So, then things will this all those stress amplitude level will go down and it will not have any sort of or kind of plateau region.

It keeps on going down. And this is stress amplitude header again. This is stress amplitude and this is number of cycle N this is S. So, that is what it is popularly known as S N curve ok in case of fatigue right. So, now this is in NaCl solution this is an NaCl solution this is in steel this is in air.

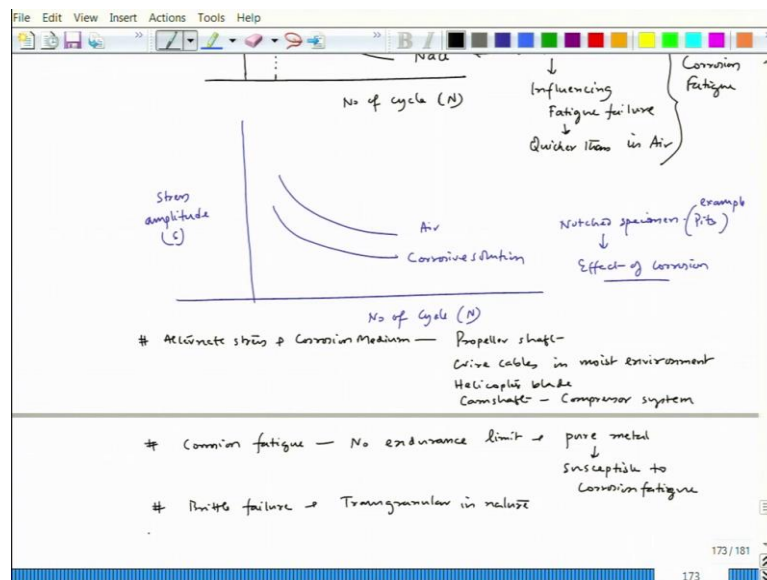
Now, you could see that the level of stress that it can withstand for a different number of cycles for example, if we take this is the level of stress what this is the endurance limit for the steel. So, that time I can find. So, that it is if this level of stress is given, it actually fails at a much lower number of cycle, but whereas, in air it does not fail, if the stress amplitude is below that particular limit ok.

So, that is what in case of corrosive solution, if the failure happens under alternate loading at a much quicker at a much quicker level ok so; that means, much quickly very much added in case of corrosive solution, the failure happens quickly compared to compared to air in air if the same alternate stress is given to the material ok.

So, that is what you could see that here corrosion is actually influencing fatigue failure and. In fact, it happens at quicker than in air. So, that is what this is called corrosion fatigue. Now, if we consider that the sample what we have taken for testing is a smooth sample. Let us say this is for smooth sample. And if we try to see the action of notched sample.

So, if in the blue color if we try to plot the notched sample that is very much possible, if the surface is not smooth if the surface has got pits, because of the corrosive solution the surface can form pits. So, those pits are acting as a sharp notch and if we have a notch and if we have alternate stress. Then, this air as well as corrosive both will drop down. So, if we try to. So, in this case, separately if we try to plot for a notched specimen.

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So, in case of notched specimen, this will drop down air and for corrosion for in corrosive solution, this will also in corrosive solution. Now, interesting part is you could see that the gap between these two is actually decreasing and the all the things are dropping down and the level of stress is also dropping down and level of number of cycles at a particular stress amplitude is also dropping.

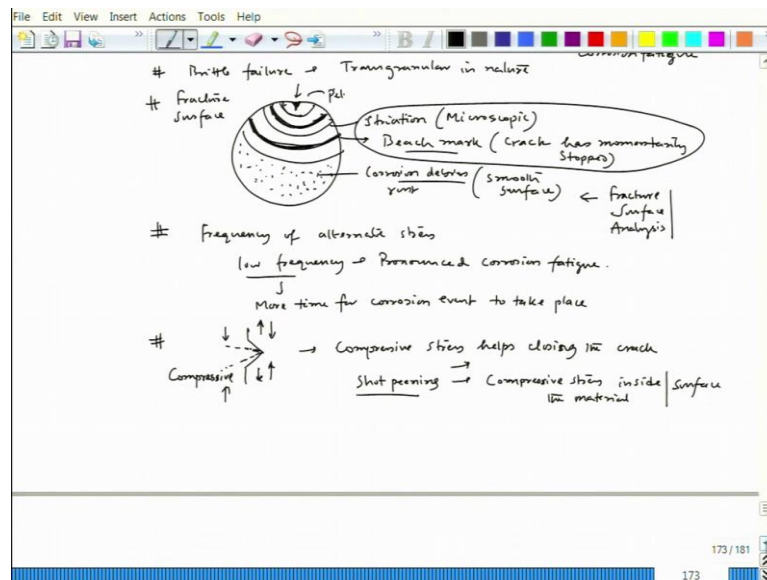
So, that is the effect of notched specimen. And it also indicates the effect of corrosion effect of corrosion, because corrosion leads to pits and those pits are acting like a example pits ok. So, these pits are acting like a notched act like a notch and that is what

the failure happens much aggressively as compared to the smooth sample when we expose it to alternate stress as well as corrosion medium.

Now, this is the corrosion fatigue part and it is actually a very very aggressive kind of failure and it happens wherever we have alternate stress as well as corrosion medium like, propeller shaft. You can also have it in wire cables in moist environment. One can have it in helicopter blades can be liable for corrosion fatigue, then camshaft in case of compressor system. So, those are the there are many other examples which are exposed to such kind of corrosive media as well as alternate stress.

Now, the major point is the corrosion fatigue there is no endurance limit. In case of corrosion fatigue, no endurance limit. It suggests that even pure metal can be susceptible to corrosion fatigue. Interestingly, if we look at stress corrosion resistance of pure metal is excellent, but once it is exposed to alternate stress, it becomes susceptible ok. So, this is a very very kind of aggressive mode of failure and mostly it is a brittle failure. And if we see the fracture surface and it is in general transgranular in nature.

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Now, if we talk about fracture surface. If we see this fracture surface let us say there is a pit small pit. So, this is the pit where corrosion fatigue initiates and from that there would be a radiating lines like this and after that this part which will be rough in nature. In most of the cases when we have corrosion fatigue, we will have corrosion debris here debris or

rust. And in most of the cases in case of corrosion fatigue, it looks like a smooth one smooth surface ok.

Now, these are if we try to look at microscopically. So, then these will be a thin line which is radiating from this crack initiation pattern and point; that is what in case of fatigue its bit easy to find out where the crack has initiated and these lines are called striation. We call it fatigue striation ok. So, this fatigue striation actually helps us to understand the point of failure ok. Now, there are some this is microscopic. And while it goes on like this it radiates like this, the fracture surface goes through.

There could be some places where you could sign you could see that there are thick zone has formed like this there is a thick zone as if the crack has stopped moving and then, in subsequent opening up stress, it will start again moving forward ok. So, this wherever the crack progress has been stopped. So, those particular things are called beach mark. So, where crack has momentarily stopped. So, those are called beach marks.

So, these are basically these two things these two things are very much characteristics of fatigue failure. So, that is what if somebody wants to do failure analysis, this is very important this is extremely important. Now so, this is fracture surface. Now, another interesting feature in case of fatigue corrosion fatigue; the frequency of alternate stress.

So, generally corrosion fatigue is more pronounced at a low frequency pronounced corrosion fatigue. This is understandable, because if we have low fatty low cycle; that means, we have more time for corrosion process to take place corrosion event to take place ok. So, this is one interesting part and. In fact, when we have low frequency the crack tip this is the crack tip let us say.

So, this crack tip we can have the ingress of corrosive and that corrosive also can actually have pitting action further pitting action or it can generate new pits. So, that way the low frequency alternate stress would lead to higher degree of corrosion fatigue. Now, the another characteristics of corrosion fatigue is if we have for example, this is the crack this is the crack you have tensile load and then second cycle, if it is a compressive load.

Now, during compressive load actually you are actually closing down. So, this is the closing down part closing down the crack. And during tensile load this is the closing part compressive which tries to close down the crack. And if it is tension, then of course, it

extends the crack. So; that means, we could see that if we somehow incorporate compressive stress it would help in nullifying the tensile action or pulling out action of the crack ok so, opening action of the crack.

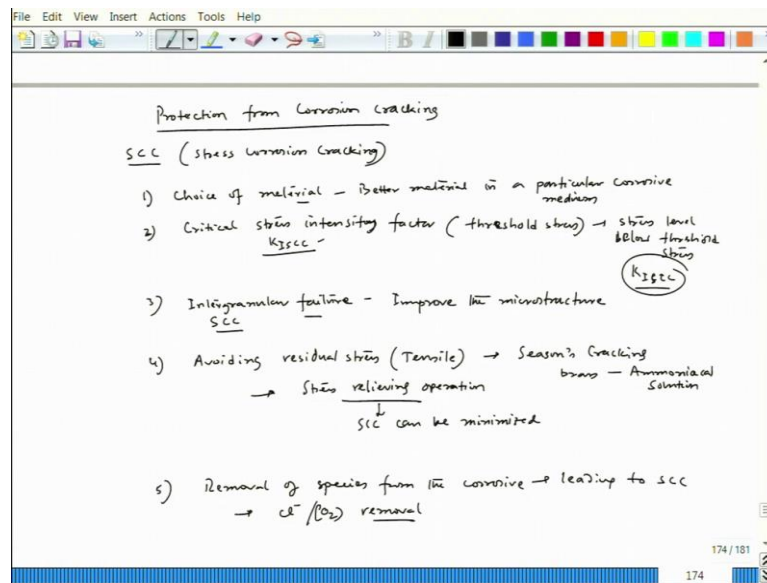
So, compressive stress helps closing the crack and this is actually that is what generally shot peening helps in preventing corrosion fatigue. In fact, you overall the fatigue is avoided, if we do shot peening; shot peening or sand blasting can help in. What we do? We are actually incorporating compressive stress inside the material.

In fact, this is done on the surface shot peening. Now, if we try to look at some of the protections. Now, these are basically in a nutshell the some of the characteristics of corrosion fatigue. And remember in corrosion fatigue, the fracture surface analysis is extremely important is extremely important.

So, that is what this kind of marks, microscopy, beach marks and flat region, smooth region and one of the major difficulty in corrosion fatigue. In case of normal fatigue, these particular marks are very visible. But let us say the corrosion fatigue happens a fracture happens and if that sample is exposed to the corrosive for a longer period.

So, this marks might go away. So, it will be difficult to understand those marks. So, that is what it is important that the sample after failure the sample is taken quickly and it is analyzed. Now, these are in nutshell stress corrosion cracking, hydrogen failure and corrosion fatigue. So, now, if we try to find out some of the protection routes how we can prevent stress corrosion cracking and hydrogen embrittlement as well as corrosion fatigue.

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So, let us look at those parts; the protection from corrosion cracking. Now, when we talk about corrosion cracking let us look at SCC or stress corrosion cracking. Now, if we try to see, we have seen that different materials behave differently in different solutions. So, in a particular solution we can choose choice of material. We can choose a material that apparently that does not show a serious stress corrosion susceptibility in that particular solution.

So, choice of material is important. We choose a better material in a particular medium better material in a particular corrosive medium. So, this is the 1st thing one can think of. 2nd thing what we know that; we know that critical stress intensity factor or threshold stress is required for SCC to happen, if the stress level can be kept below this so; that means, this is K_{ISCC} .

So, this one if it is kept below the stress level where this particular factor is below the critical value where stress corrosion does not happen. So, then we can avoid stress corrosion cracking. So, that time stress level is below threshold stress which is coming from K_{ISCC} ok. So, that we can we have already discussed.

Now, 3rd is; since most of the cases it actually many of the materials it goes for inter granular failure and that we have seen happens due to the precipitation along the grain boundary or solute segregation along the grain boundary. And those solute segregation segregated grain boundary could be active or could be cathodic compared to the

surroundings thin region of the grain boundary or those precipitates could be cathodic and the surrounding region could be anodic.

Just like in sensitized stainless steel where chromium carbide precipitation along the grain boundary makes it susceptible to inter granular failure and that can also lead to inter granular fracture due to the action of stress. So, that means, if we try to avoid inter granular SCC. So, we can say inter granular SCC somehow, we improve the microstructure.

So, like avoiding solute segregation along the grain boundary or solute precipitate formation along the grain boundary like SCC like inter granular corrosion of stainless steel 304 stainless steel can be avoided by avoiding carbide precipitation along the grain boundary or solutionization treatment or by adding elements which will take care of carbon; so that chromium carbide does not form and chromium remains in solution and keep giving better corrosion resistance.

So, this is one route by which stress corrosion cracking can be avoided. Then, 4th is of course, avoiding residual stress. And here, it is basically tensile component that leads to stress corrosion cracking; example, we have talked about seasons cracking in case of brass ok.

So, of course, their environment is ammoniacal solution. So, that particular thing is coming due to residual stress like example brass casing over bullet. Now, if that is actually this residual or stress relieving operation is done. So, then this residual stress would go off and then, SCC can be minimized fine.

Now, one can also look into removal of species from the corrosive leading to SCC; like, when we see stainless steel piping in boiler cooling water piping that is actually susceptible to SCC, but if we remove chlorine, iron as well as oxygen dissolve oxygen. So, there that particular SCC of that piping system can be avoided.

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5) Inhibitors
→ Cl⁻ / O₂ removal

6) Inhibitors
7) Cathodic protection

8) Protective coating

Hydrogen Assisted Cracking

1) $H^+ + e \rightarrow H$ → H_2 → $2H^+ + 2e^-$ → $2H_2O$
Phosphorus As → Hydrogen poison
Avoidance of poison (Hydrogen)

2) Avoiding cathodic protection, eliminating galvanic couple

3) Removing H from metal → Baking ~200°C

4) Better material → Monel, Hastelloy C-276,

5) Use of better filler material or electrode (low H content)
→ Dry atmosphere (H₂) → welding → avoids Hydrogen ingress

6) Acid pickling ← Use of inhibitor

So, that is another aspect one can follow. 6 inhibitors can avoid SCC use of proper inhibitor. Then, use of cathodic protection that can also avoid SCC, but remember in this cathodic protection, one has to be very clear. If it is anodic if the mechanism follows anodic dissolution, then the cathodic protection helps, because once you give negative current; that means, it does not allow that dissolution to happen.

But if that material is susceptible to hydrogen induced cracking or hydrogen assisted cracking, then the cathodic protection should be properly used or carefully used, because if there is hydrogen evolution in those cases that hydrogen can lead to hydrogen assisted cracking. So, cathodic protection must be used where anodic dissolution-based mechanism is followed, but that material does not show hydrogen assisted cracking. So, that time cathodic protection helps.

Now, 8th somebody people can use protective coating ok. So, like if somebody uses a protective coating which does not allow the heat to does not allow if we use a protective coating which does not allow hydrogen diffusion to happen ok. So, then hydrogen assisted SCC or hydrogen assisted cracking can be avoided.

But that does not fall under typical SCC, because their hydrogen is playing a role there, but that protective coating can also prevent SCC. So, this is about some of the protection used for SCC prevention. Now, one comment I have that is if we talk about hydrogen

assisted cracking as well as SCC, in both the cases you need static load or tensile load. Now, that load should can be much below the yield load of the system.

Now, hydrogen just like another there was a mechanism called adsorption induced decohesion model. And in that adsorption induced decohesion model, we saw that the liquid metal can go into the diffuse into the material and then in the crack tip zone and reduces the bond strength and which is actually leading to decohesion and then crack can go into the material.

Now, just like decohesion there is a decohesion model available for hydrogen also, which actually diffuses into the crack tip and then reduces the bond strength or reduces the surface energy and that way cracks crack that stress required for cracking also reduces ok.

So; that means, hydrogen is actually acting as a kind of helping agent, but the stress is playing and hydrogen. Why hydrogen is coming, because of the corrosive reaction. So, that could it could be that hydrogen assisted cracking could be a part of SCC, but since hydrogen is involved.

So, that is what it has been separately counted as a hydrogen assisted cracking. Now, in case of hydrogen assisted cracking, following can be considered for protection against hydrogen assisted cracking. For example, we see that hydrogen generates in acid medium or water can be reduced. So, these two reactions can lead to hydrogen.

Now, this hydrogen if it finds another hydrogen, it goes to H_2 and then that bubble goes out from the system. But there are some of the species for example, phosphorus containing ions or arsenic containing ions. So, those actually act as hydrogen poison and that poison actually does not allow this combination reaction ok.

So, if that combination reaction is enhanced, then hydrogen assisted cracking can be avoided to a great extent so; that means, avoidance of poison or we call it hydrogen poison would avoid hydrogen assisted cracking, because atomic hydrogen would not stay longer in contact with the metal surface. So, it will combine another with another hydrogen and form hydrogen gas and once it forms hydrogen gas, it does not diffuses in ok. So, this is one part.

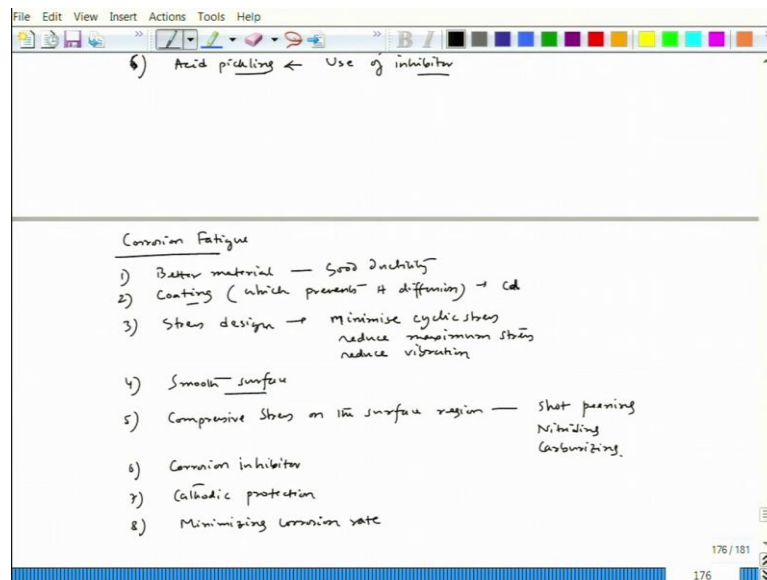
Then of course, one can use one can think of avoiding cathodic protection, where we know that, that material is susceptible to hydrogen assisted cracking. So, that case it can actually avoid hydrogen assisted cracking or hydrogen embrittlement even. Now, we can also see avoiding. In fact, we think of avoiding cathodic protection we can also think of avoiding galvanic couples or eliminating galvanic couple that can prevent hydrogen assisted cracking better material.

And in case of that one can use Monel you can one can use Hastelloy C 276. So, these are the kind of alloys on mainly nickel based alloys, they are good in terms of having high resistance against hydrogen assisted cracking. Then, use of better filler rod filler material or electrode which actually has low hydrogen content, as well as if we can use a better shielding gas which avoids presence of moisture so; that means, a dry atmosphere where moisture is not present moisture is not present.

So, if we do that welding if that condition welding is done. So, the material will not pick up hydrogen and hydrogen assisted better welding. So, use a better and dry condition welding avoids hydrogen assisted cracking hydrogen. In fact, it avoids hydrogen ingress during welding and that automatically avoid avoids hydrogen assisted cracking.

6; one can think of during acid pickling this hydrogen assisted cracking is quite often noticed. So, that is what proper flushing of hydrogen or use of inhibitor which allows hydrogen formation gas formation that would help that definitely helps avoiding hydrogen assisted cracking ok. So, these are some of the routes where hydrogen assisted cracking can be prevented. And finally, if we could see the preventive measures for avoiding stress corrosion not stress corrosion fatigue.

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So, there are couple of measures one can take. So, corrosion fatigue. So, 1 is better material and better material means good ductility. Coating, which prevents hydrogen diffusion. In fact, nowadays that petroleum industry where hydrogen assisted cracking is observed those low carbon low alloy pipeline steel.

So, in those cases people are thinking of having coatings people are thinking of having nickel phosphorus coating or cadmium coating. Those help actually those actually increases the resistance to hydrogen diffusion into the material. Then of course, stress design. So, which actually minimize cyclic stress, reduce maximum stress and of course, reduce vibration fine. Now, we can see that notched specimen has got a higher susceptibility to corrosion fatigue. So, the smooth surface can actually lead to higher resistance to corrosion fatigue.

5; as we have seen that compressive component closes down the crack tip. So, that is what compressive stress on the surface region. It actually prevents corrosion fatigue and that can be done by shot peening. Shot peening is a process where one can actually introduce surface compressive stress. People are also can use nitriding or carburizing. So, that way one can also avoid corrosion fatigue.

Protective coating; as I have told that when you talk about coating. So, I miss that point one can use cadmium coating on steel. And nowadays, people are also thinking of putting nickel phosphorous coating on line pipe steel. 6 is corrosion inhibitor. So, that

can also avoid corrosion fatigue. Now, cathodic protection can be employed. And finally in fact, one can think of minimizing corrosion rate overall corrosion rate.

So, that can also prevent corrosion fatigue and interestingly in the case of corrosion fatigue, one has to look for surface marks as well as pits, if they are forming due to corrosion. So, those are the points which are vulnerable and they are from corrosion fatigue crack can initiate So, these are some of the protective routes or methods one can employ to prevent corrosion cracking in general ok.

But different three different method different, different routes of corrosion cracking. One is corrosion fatigue hydrogen assisted cracking and stress corrosion cracking. They have somewhat little different approach to protect, but most of the cases one thing is very sure that if you can prevent corrosion, then the stress factor is also only there. So, then our life would be bit easy ok.

So, let me stop here this module that corrosion failures and analysis. There are several other corrosion failures that you can look for in internet and then try to relate with this kind of mechanism what we have analyzed the kind of corrosion different corrosion processes what we have analyzed ok.

You would see that many of the cases you would be able to understand the failure routes and once you know the failure routes, it will be easy to find out the protective routes or protection routes also ok. So, that is what one should aim for if somebody is a corrosion engineer ok.

So, let me stop here. And this particular module is initially I thought that it will be 40 lectures. Now, we have gone up to 42, but still many things are not told, but you have to also do a little bit of self-study and understand this particular important aspect of corrosion failures and analysis. Now, of course, there will be modules on corrosion testing, as well as protective routes. There are several protective routes like.

We have just talked about protective routes like when we talked about different corrosion forms like design, materials, environment, then electrochemical potentials which can be done either by anodic protection or cathodic protection and there are other there are inhibitors. So, there are majorly five routes ok. So, those routes will be tackled or will be

considered in a separate module which will be around 10-hour module. And also, there will be a one more module on corrosion testing. So, till then we stop here.

Thank you very much.