Aqueous Corrosion and its Control
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Lecture – 29
Forms of corrosion: Stress corrosion cracking (Part-I)

Welcome to the discussion on one of the most important topics in Corrosion of Metals and Alloys. The topic of discussion is a Stress Corrosion Cracking.

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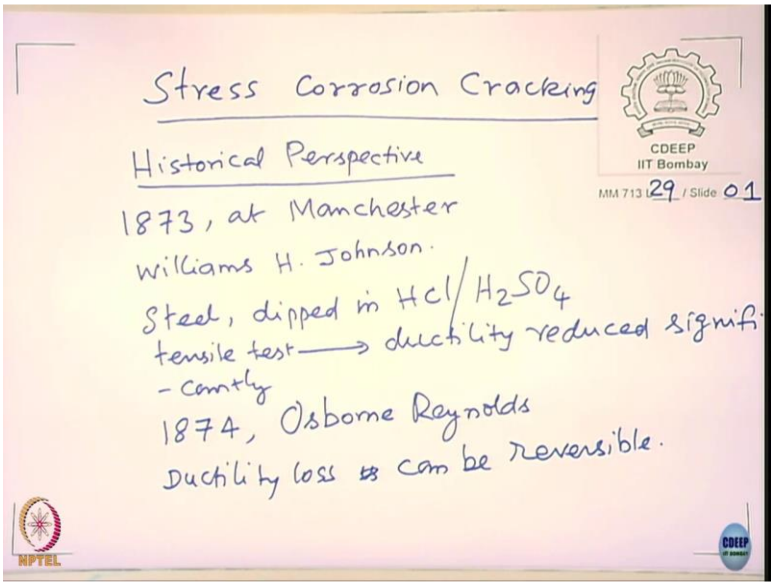

So, far we had looked at the corrosion of metals for perspective, where there are no applied stresses acting on the metal. We discussed the galvanic corrosion, where you had dissimilar metals coming in contact with each other electrically. And we said that the anodic member of the couple will undergo the corrosion aided by the cathodic member.

We then, went on to discuss the crevice corrosion in the structure, when you form a crevice because of the fabrication issues, the crevices act as sites of corrosion. We looked at the passive metals and we said that the passive film can break down under certain conditions may be a mechanical damage or it could be due to the specific ions present in the environment leading to pitting corrosion.

Then, we looked at what happens when there are the transformation in the material, especially in stainless steels that leads to sensitization. We looked at the inter granular corrosion of the stainless steel and these relevance to welding and fabrication. The inter granular corrosion again not only confined to stainless steels, it can happen in any other material more so in magnesium alloys and aluminum alloys and copper-based alloys, when the grain boundaries are becoming electrochemically active.

They are all in all these cases we also assumed that yeah, there are one more case we also discussed where, we call as selective leaching and de alloying. In all these cases we assumed that the environment is static in relation to the material and we looked at what happens if the environment moves in relation to the structure to the material.

Then, we had looked at three different forms of a corrosion and flow assisted corrosion, erosion corrosion damage, the cavitation damage we talked about where the environment, we consider was the fluid. It could be a gas, it could be a liquid and of course, in all these cases you can have a suspension of the solids; but essentially, it is a fluid.

We looked at one more case, where the contact surfaces are in motion ok. In the contact surfaces in this case are a solid state right, they are a solids; one metal against another metal and one metal against another ceramic. For example, when they are relatively moving and when they are under load conditions, what kind of corrosion it occurs. We called them as a fatigue damage.

The loading condition that are acting on this on these contact surfaces only you know they are not consider in terms of what happens in the bulk; the load, the stresses that happens in the bulk, we are not considered. In fact, these you know contact surfaces the interfacial loading is the predominant factor. But you know most often, the engineering metals and alloys are made for structural applications.

They bear the load right, beat, a shape, a pipeline or a reactor, it could be a pressure vessel for example or could be aircraft or I mean you can name quite a few actually. In all these cases the metallic structures are experiencing certain amount of stresses. You can also start classifying stresses in the different categories; it could be a tensile stress, it could be a fatigue stress or could be a sheerly a torsion test you know stress can happen.

So, when you have this, when you also have an environment acting on the surface, the failure mechanisms are different and they have very serious consequence. In fact, you would see that the metal hardly corrodes in terms of visible changes, loss in weight is hardly seen at all; but it can lead to cracking, it can lead I mean as a result of which it can be leaking and you know and structural instability and there could be safety issues involved.

So, what we are going to look at in this particular may today and in a couple of days is how a metal under tensile loading condition and also exposed to the environment respond to it ok. What is the mechanism of such corrosion process and what are the factors that affect such kind of corrosion and how do you prevent them and if there are any kind of fingerprints, characteristics of that form the corrosion is also important. So, these aspects we are going to see. So, before I go into it, I just want to show certain illustration, how the corrosion can really affect in practice.

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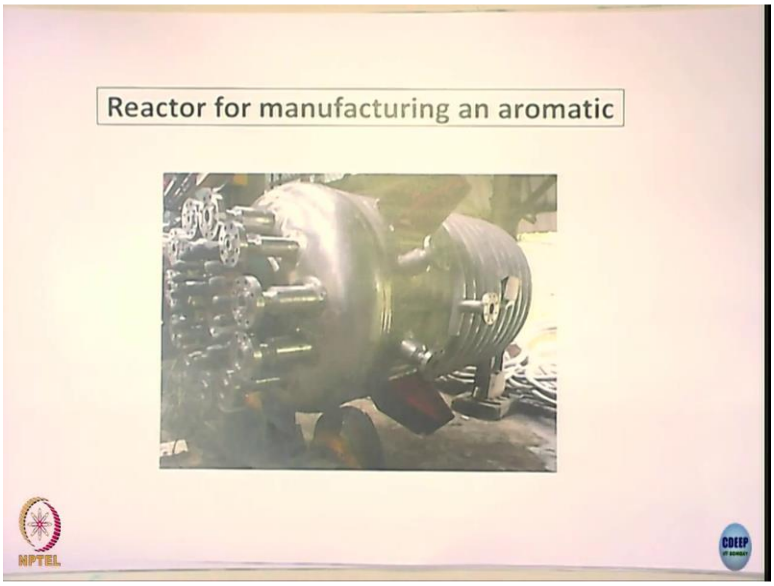

This in fact, is an ongoing work which we have been do we are doing now. This is the reactor, in fact is a pressure vessel I would say. It is high pressure. It is meant to produce an aromatic compound you know most of you know the aromatic compounds are you know as a special characteristics. And they are synthesized using inputs which are mostly organic and may be some time, you may add sodium hydroxide, you need water. You are subjected to high temperature, high pressure conditions.

The reactor that you are seeing here, do not worry about all these inlets-outlets, all these stuffs actually; because there are you see they feed hydrogen, you know when you feed hydrogen; then, there are lot of precautions that you have to take cannot simply do it. So, there are so many ports.

It was made up of a 304L stainless steel. The company wanted to increase the production, they went from a smaller reactor to a bigger reactor in just 4 months; just 4 months of his inception, commissioning ok; the reactors start leaking and I do not think you know when your hydrogen you really would like to take risk of that actually and if you if I look at it; look at the inner walls of the reactor, normally you do NDT right.

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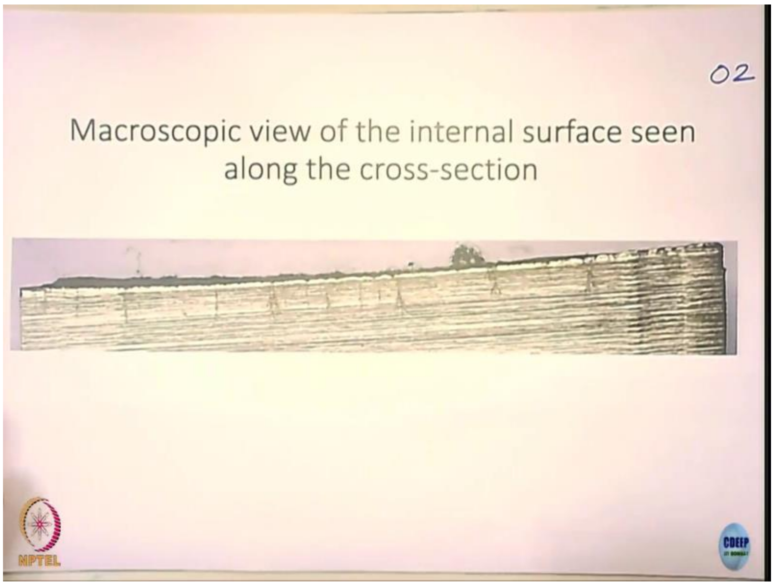

NDT is one very versatile; NDT's are dye penetrating tests, some of you as be aware of it right. You apply a dye on the on the surface and you have wipe them out and you can just you know you also add another elutant to the surface and so, the dye comes to the surface and wherever the crack, the dye penetrates and comes back to this. So, you will able to see this you know the subsurface cracks, even surface cracks using the dye penetrate test.

When you take a cross section of that, you see how the cross section looks like. I do hope you will able to see very fine cracks, starting from the surface and moving towards this. It is a very thick vessel of 50-millimeter thickness. It is a 304L stainless steel and you find that it just failed in 4 months.

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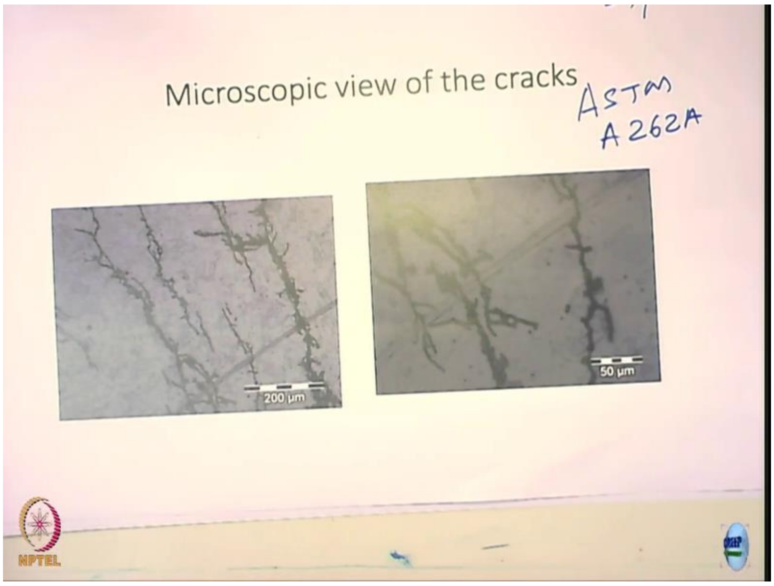

If you look at little bit more in detail at a higher magnification and you would find the cracks are microscopic in nature and the microscopic cracks turned into a macroscopic failure. And you guys now are reasonably familiar with metallurgy, you see that these cracks are all branching now and you see some of them are called trans granular cracks ok. We come back to this soon. So, 4 months time and the reactor started failing.

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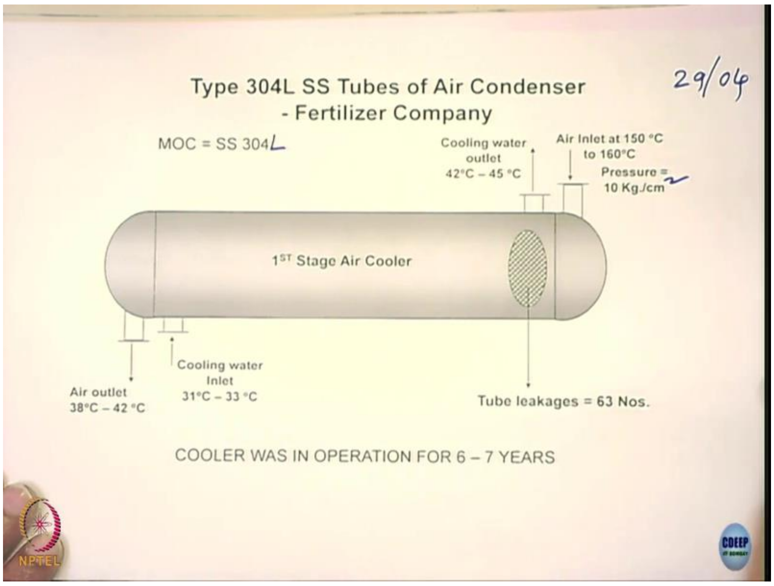

This is an heat exchanger ok, you know it is a kind of schematic of that and it is called as a Air Condenser right. You want to dry the air, so you need to you know and you know especially, when see what happens you know in industry every heat is important right. You when you create heat, you just do not want lid out right. You take the heat out from that ok, heat is essentially energy right. So, the air comes out of the reaction process, you need to remove the heat because it cost money and this is a its a condenser right, air condenser right. It takes the heat and it is called as a cooling water system ok.

So, what you do here is that you can see here that there is a inlet here ok, it goes inside, this outlet here and it is a horizontal heat exchanger. And its made up of a 304L the stainless steel, the air inlet the temperature is about 150 to 160 degree Celsius at a pressure of 10 kg you know centimeter square and you have a cooling water you know enters here and comes out, air enters here and then we comes out here ok. It is a counter current process right. It is what happens.

The material used was 304L stainless steel, it is a fertilizer company and the cooler in operation was for 6 to 7 years; may not longer. And the tubes which are inside, 63 of them started leaking at all actually, that was a problem essentially. You have premature failure right, you just take these tubes and see the tubes in a you know in a microscope.

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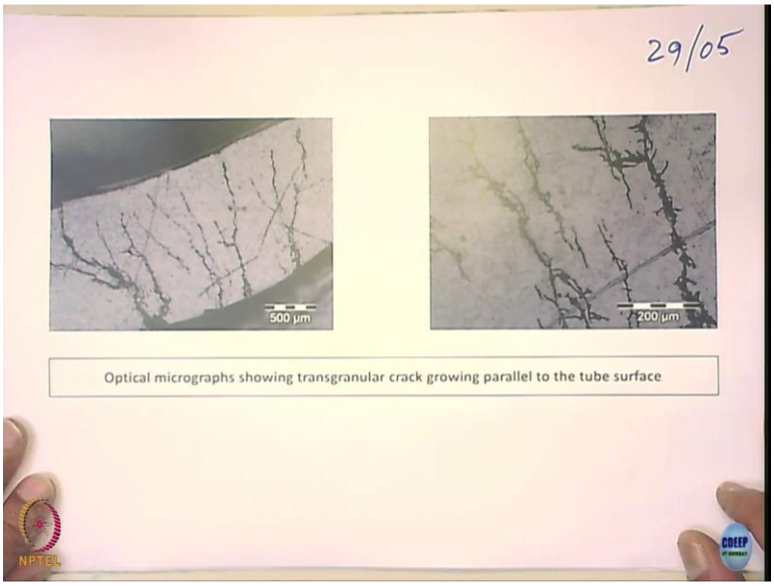

This is the cross section of the tube, you see here the cracks started from the external thing, where the water went through the water went through this ok. So, from wherever the you know, because the surface is you know is covered with water and you start you know cracking. This is called Cooling water; this is not a distil water. It is of course, a pure water; but not like your dm water. Again, you see a kind of branching of cracks, this is one of the characteristics of stress corrosion cracking and if you know you know if you do a tensile testing or if you do a mechanical loading, it s a failure. You only see a one crack; the cracks are not branching at all. The crack morphologies, we will discuss shortly and this is also a some kind of a trans granular cracks taking place.

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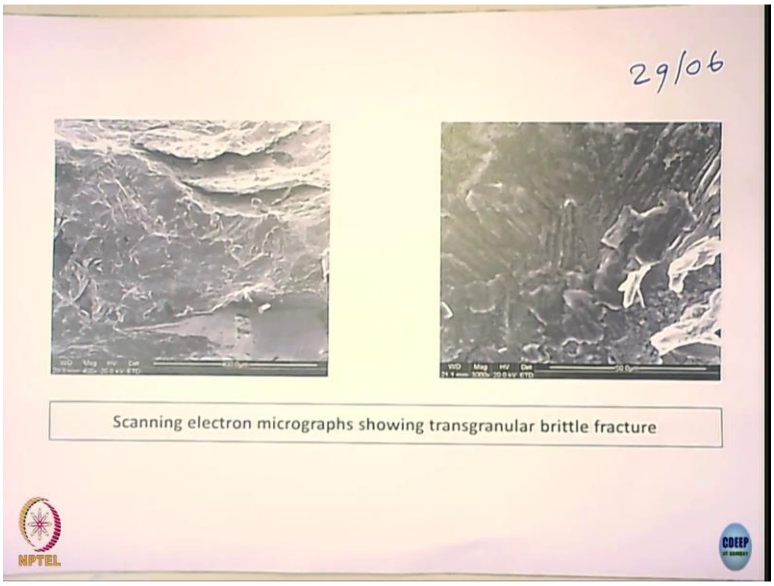

Look at this in a scanning electron microscope in detail; see the surface is the surface is quite brittle surface right. It is a brittle surface; it is a brittle surface. And those guys who are with the metallurgy background, you would appreciate, you will able to understand what brittle fracture is and those who are not from the metallurgy background, I want to show how a normal fracture should look like in scanning electron microscope ok.

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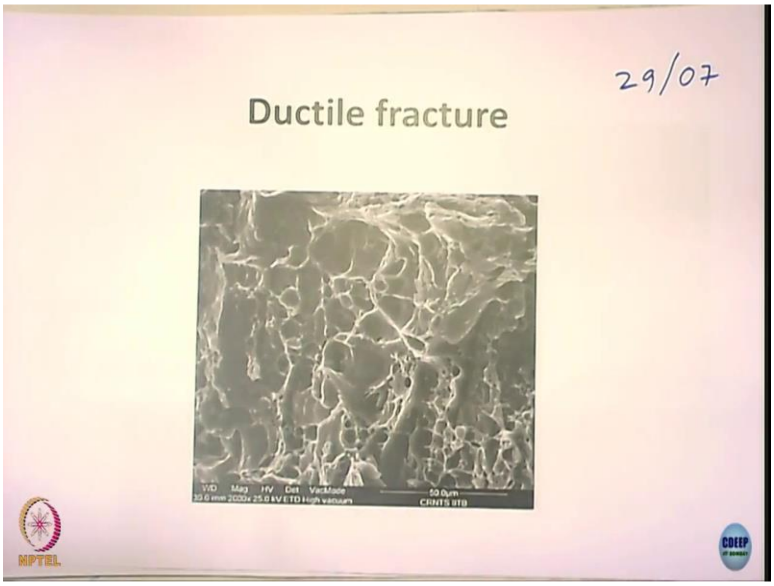

You see this here; this is a material failed in air in the absence of environment. it is a tensile failure and hope, you can see this is called a fibrous failures, it is called a dimple failure and dimple fracture and you can see the fibers you know, the metal as nicely elongated; they are they are just flow nicely flow right.

So, this is the kind of ductile fracture, you see when you have; when you have you know simply failure in air. Suppose that it looks like a glass just failed here ok. So, the problem in stress corrosion cracking is that it can cause a premature failure and it can lead to certainly see, it is not going to cause too much of corrosion see here.

Now, the surface ok; this is the surface internally and you do not really see much of corrosion at all. I hope you were able to see this clearly. Now it is its almost, but then wherever there is a crack, crack can happen and in subsequent place you are not seeing any corrosion.

So, visually they are not undergoing severe uniform corrosion at all and so, this corrosion is very localized and it is called as a stress corrosion cracking. Now, stress corrosion cracking has been a really a problematic thing actually; it is a is a problematic thing. And in fact, if you look at the history, historical perspective of that, I am not going to discuss there is a paper by (Refer Time: 17:19).

I think give a reference later and he has given very nicely the history of stress corrosion cracking. Actually, in the year 1873 at Manchester, so guy called Williams H. Johnson, he did a very interesting curious experimentation. What he did was he took steel and then, it dipped in hydrochloric acid and also in sulphuric acid; both the acids, he did a nice just dipped it and then, he carried out a tensile test. He found ductility reduced significantly.

In the year 19 sorry 1874, there is another interesting person and Osborne Reynolds, he did a very another interesting experiment. He found that ductility loss is can be reversible. You expose it to the environment and do tensile testing and you see there is a loss in ductility. But you just leave it for quite some time in air. He says that you do a test after few months and a major part of the ductility loss can be recovered actually that was a very interesting experiment that was done.

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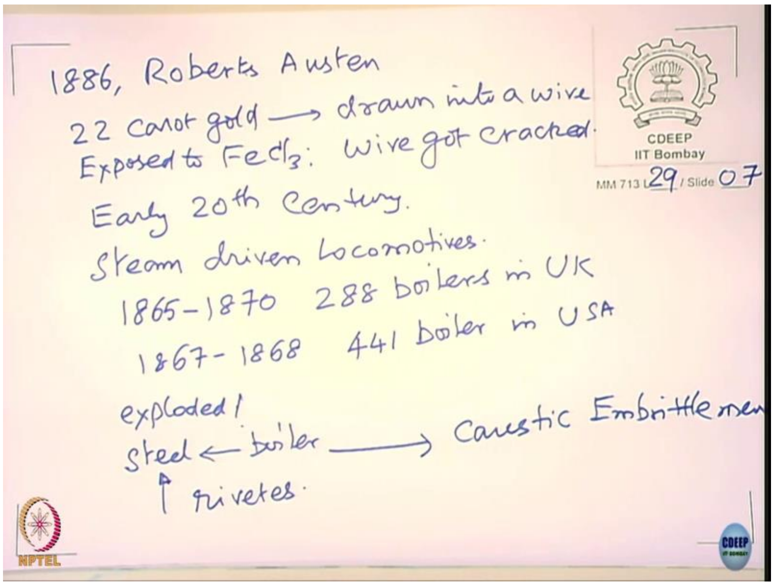

Now, subsequently and in the year 1886, the guy called Roberts Austen, what he did was, he took a 22 carat gold and drawn into a wire right and then, he exposed to ferric chloride, wire got cracked. Probably this is where the first you know such observation which talks about the so called stress corrosion cracking. The earlier observations, they pertain to hydrogen damage hydrogen embrittlement, we will talk about later.

So, they were all academic experiments, they are all they have more academic and the importance of such kind of loss in mechanical properties; you see what is here? There is a loss and ductility taking place. You are not realized. They started realizing it in the early 20th century. There was a time, where there was industrial revolution taking place right. Lot of you know technologies were developed actually and it so happen, the invention of steam driven locomotives right. The steam driven locomotives first saw the problem of stress corrosion cracking. How severe it can be right. Now, it is simple water and you generate a steam and that is used to drive locomotives. Now, which is used same steam is used now to generate electric power right. Now, people have this electric powers.

Now, this is a problem because you see here this is very mind boggling 1865 to 1870, 288 boilers in UK and in 1867 to 1868, we had 441 boilers in USA exploded. It was really kind of you know and you know you see the consequence of explosion right. The pressure vessel actually in the steam at that temperature pressure lot of casualties actually. How that happened? The steam locomotives made up of steel; I mean not locomotives, I am sorry, the boilers made up of steel and they are fabricated using what? How they fabricated? Using rivetes right.

What is then? You put a seed and then, you put a rivet and then, you just what you cold compress it right. There will be more stresses. There will be lots of residual stresses in the system and you know when you when you use water for the boilers, the pH is increased; otherwise, what happens? The steel will corrode right.

The pH used to be around about 10 or so and then, what happens when you when you boil the water, you take the steam out, what will happen to whatever remains in the boiler? How do you make the pH of water higher? You add sodium hydroxide right and you increase the pH with let us say 10 and you boil and evaporate.

So, what happens now? With the time the sodium hydroxide concentration increases and then, it leads to cracking. So, that is the name emerged, we called as Caustic Embrittlement. The caustic embrittlement now we are all know that it is simple mechanism of stress corrosion cracking right.

But those days, they call a caustic embrittlement because wherever the caustic accumulated, see what happens when you have a sheet and then you join them like that right, join them like this and you put a rivet, you put a rivet here ok. And this gap there be accumulation of the accumulation of the sodium hydroxide and start giving rise to crack.

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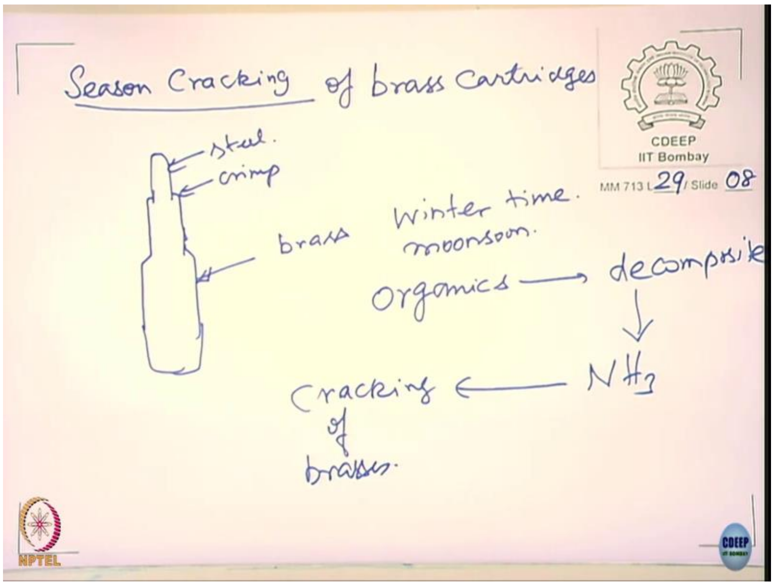

Historically, there are one more incident that was that also brought the attention of the people, Season cracking of brass cartridges. You know it is a bullet right and you mount a you mount a bullet right. You crimp here right ok. This is hard one may be steel or something like that ok. This made up of brass.

So, they you know what happened was the cartridges started cracking during the winter time. See they were stressed to India first actually because the British found that. They found that this cartridges failed during the, during winter and monsoon time, you know winter and monsoon time, where you know what happens to organic?

Suppose, you have a organics, they decompose and then, they generate ammonia. The ammonia cause cracking of brasses. So, these are the names given to stress corrosion cracking because they are associated base certain events and they are all in fact can come under stress corrosion cracking of metals. Why is that you should worry about stress corrosion cracking.

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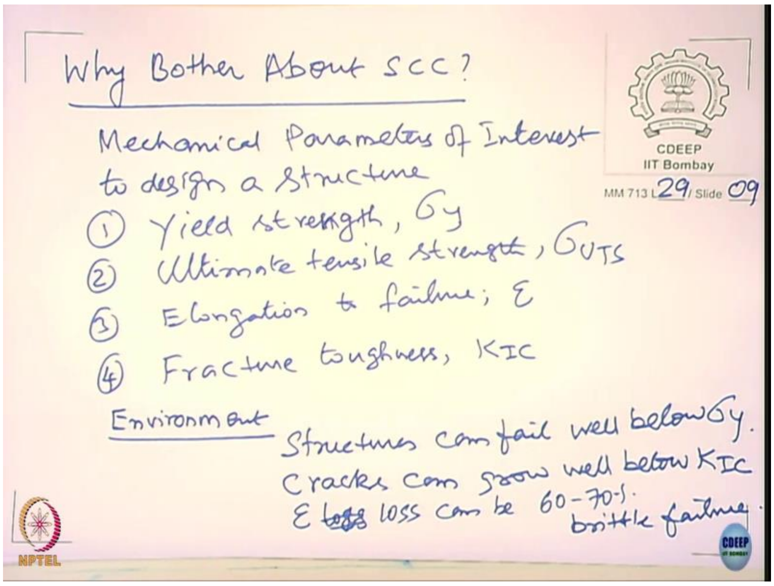

Why bother about stress corrosion cracking? We have I think some mechanical engineers right background right. I think I give a material and I ask you to use that material to design some structures say maybe a pipeline or maybe a foot over bridge, whatever. So, what input parameters do you take to design the structures? (Refer Time: 30:26) the material right. Of course, it has to take certain load. So, the loads are given to you. So, what input parameters of the materials you would consider?

Student: (Refer Time: 30:42).

Yeah?

Student: Yield stress.

Yield stress?

Student: Yes.

Yield strength right then?

Student: Force strength.

Ultimate tensile strength, then you look at the ductility in terms of the elongation right, these parameters. Of course, you can also look at a toughness this is K1C value and do that right. So, you look at the yield strength of the material, ultimate tensile strength of the material, look at the elongation that happens at all and then, you can look at the K1C value which is called as a the toughness. So, the parameters the mechanical parameters of interest to design a structure; one it could be yield strength, two ultimate tensile strength, three the elongation to failure right failure, four the fracture toughness. If you design a structure, wherein the load does not cross the yield strength of a material right.

Suppose, I use a steel and carbon steel was what may be a 200 mega pascal, 250 mega pascal is the carbon steel strength right, yield strength and ultimate tensile strength may be about 400 mega pascal something like that and the elongation may be around about 18 percent say range of things I have.

So, suppose, I design a structure such that the load does not lead to a stress level beyond the yield strength of the steel, What happens? It will endure, it will endure forever because it is within the elastic limit. It does not undergo any plastic deformation right. It is within the within the elastic limit. So, it supposed endure for long term, suppose you have an environment coming in contact with this, structures can fail well below yield strength.

It can it can happen even at about 25 percent, 30 percent of yield strength and not all cases; I am saying there are cases, where the metal can fail all about 25 percent, 20 percent of the yield strength. Now, crack can grow cracks can grow well below K 1C, fracture toughness is K 1C right. Elongation is given as epsilon, sigma UTS and sigma yield strength. That is because the elongation loss can be 60 to 70 percent, I can know I can lose my elongation 60 to 70 percent. So, what does it mean? If I lose that elongation that is what is mean by elongation means what?

Student: Ductility.

Ductility right. The ability of the metal to manage in his distortion in the structures that could happen during the load bearing things, is not it? It could happen right. So, if there are one-way distortion and if the metal is not plastically deforming, then what happens like a glass, it going to just simply crack. So, you can lead to a brittle that only talks about the safety right. The safety here is depend upon how ductile, how tough they are actually

So, if it is going to be a brittle then safety becomes a casualty. So, stress corrosion cracking is a problem and for the structures, where you expect it could suffer ok, it could suffer. So, that particular failures. Then, look at what is stress corrosion cracking?

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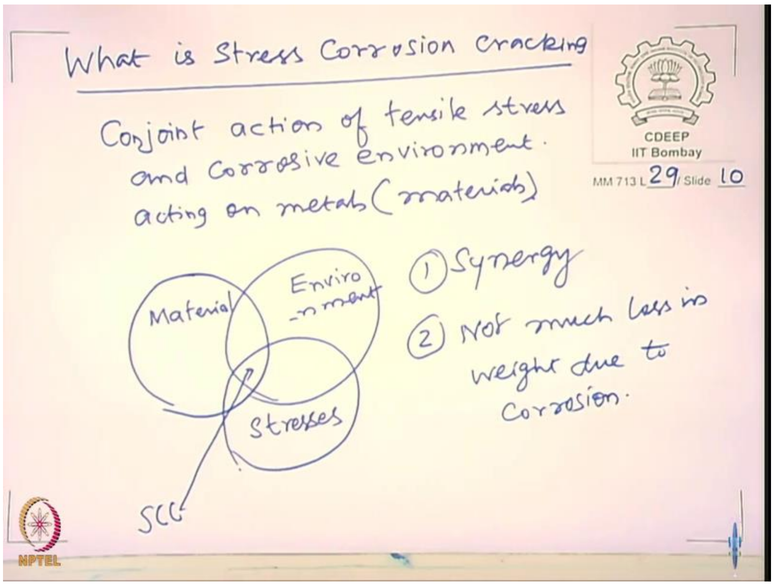

It is conjoint action of tensile stress and corrosive environment acting on metals; can also happen in materials also. It can happen even in glasses; it could happen in polymers right, most of the engineering materials we you know we deal with and especially, this course we discuss more on metals ok.

But it is just not confined only to metals and alloys, materials can happen. Ceramics can fail, glasses can fail, polymers also can undergo, stress corrosion cracking because the environment can interact with them.

So, you have three players here; one is material, other is the environment, I is the stresses; I mean stresses I mean here that tensile stresses. It is not a fatigue it is not a fatigue stress, not a shear or I mean we are not talking about torsion and we are not talking about you know compression, all these kind of the things and all these lead to SCC.

So, it is a synergy taking place. Please look at it is a synergy right. It is its not a cumulative that corrosion means this much loss and weight. In air, the metal undergoes this much of tensile strength; it is not additive, it is a synergy and also not much loss in weight due to corrosion. Now, this is a Venn diagram; (Refer Time: 40:12) is Venn diagram.

Now, you look at this there are three players here; the material, the environment, I mean the chemical environment here. I suppose we define the beginning of the course itself, we are not talking about physical environment; we always talk about the chemical environment, when it comes to corrosion and we are talk about the tensile stresses. So, in order to understand stress corrosion cracking, we need to look at the material aspect, the environment aspect here and we need to also address the stresses.

So, all three we need to be understanding in order to get a picture about stress corrosion cracking and then, to say how we can control the stress corrosion cracking. Stress corrosion cracking can be taught maybe some 10-12-15 lectures more actually. So, we will be very brief and you know at best, we will take about 3 classes and try to see you know how we can understand stress corrosion cracking of metals and alloys.

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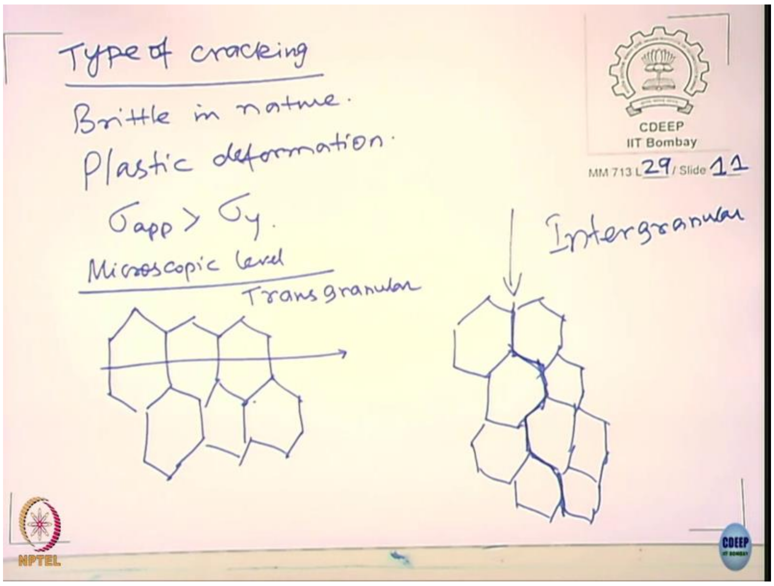

Now, let us go into the first aspect of the cracking. The types of cracking whatever be the cracking, whatever be the types of cracking? The cracking is always brittle in nature. A brittle is a very qualitative term, you know it is very difficult to define what a brittle is right. I do not think this can be say anything which is 100 percent brittle and you cannot say anything as 100 percent ductile kind of things. So, it is a character of the material actually. What is the character here? What is mean by brittle as opposed to ductile? What do you mean by that? Let us look at from the perspective of what happens to the metal, when you deform it actually right.

Student: Sir, can we say that brittleness is that there will be no elongation before the crack propagation can take place?

So, there will be?

Student: No elongation.

What is mean by no elongation right ok; what do you mean by no elongation?

Student: Local yielding at the surface.

There is no local yielding at the surface ok, more alright you are right and what does what is happening that means? There essentially, there is no atomic mobility taking place essentially in the success. When you apply a stress, the atoms start moving that is what you call a plastic right. You call a plastic deformation right? It is a plastic deformation we call it. When does the plastic deformation occur? When the stress applied is greater than the?

Student: Yield strength.

Yield strength, that is where the dislocations move. The atom move you know the mobility of atoms are related to the mobility of the dislocations right. So, only above the yield point, dislocations move and through which the atoms move and so, there is going to be going to be plastic deformation. The metal take the shape that you wanted right. In the elastic limit, there is no atomic mobility is not going to be there. If the metal fails in the elastic region, then it becomes a brittle ok. Why? Because there is no; essentially atoms do not move at all.

If the stress corrosion cracking the environment facilitates the crack initiation and crack growth below the yield point, then what happens? Then, the metal will behave something like a glass because they do not really move at all. Am I right or not? So, the fracture process depends upon at what stress level the metal fails.

If it fails close to ultimate tensile stress, then what happens is going to be nice full ductile. It will face in somewhere between the yield point and UTS depending upon where it fails, the extent of ductility is going to change ok. So, it is a qualitative parameter. I do not want to you know discuss too much on it ok, but I want you to get a feel for that right; that means, if the metal can fail below yield point, you can get nice brittle cracks occurring on the metals. But not necessarily always the metal fails in that manner.

Now, let us look at a microscopic level, how does the crack propagate that is a macroscopic level right. And a microscopic level, how does the crack propagate? We all know we deal with poly crystalline material right. Now, the crack can grow along this way, we call it as trans granular crack.

In fact, the most of the mechanical failure happens in the air are all trans granular cracks; but they are trans granular ductile cracks ok. Here, you also have you know trans granular, but then these are trans granular brittle fractures; the crack also can grow ok. It can grow along and what is this called? Inter granular cracks.

I will go back to the some slides which I have shown you before so that you get a clarity in terms of what is mean by trans granular cracks and inter granular cracks. I hope this is the slightly at higher magnification, lower magnification. This is at a higher magnification. Now, hope you were able to see the grains here ok. Now, look at this is the crack grows straight you know cuts across all the grains. So, its it is a trans granular cracks.

So, is here you see that in this scanning microscope, it is it is it is it is the please look at this is the this is the this is not the crack interface right. You can break open this. This is a crack plane; this is a crack plane nah it is a crack plane in the this is a plane through which the crack is moving now. Now, look at this; this becomes totally trans granular cracking and I hope you are able to see some grains here, grains here; there are grains here, there are grains here. Now, you can see this also this is a grain here.

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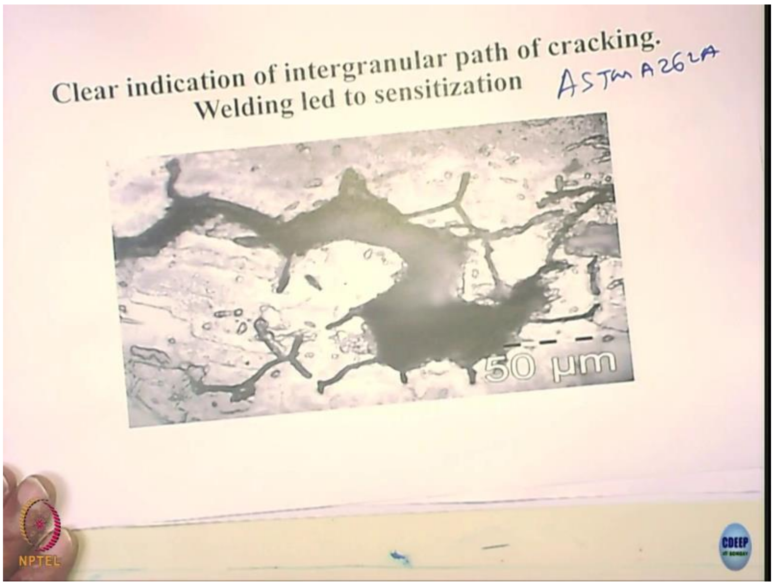

So, the crack cuts across the grains. So, they become trans granular cracks in natures. Look at this and it is a clear inter granular cracks ok; look at the grain here, the grain here, crack grows along the grain boundary ok. Why? The grains are got sensitized. You can see this here, the grains got sensitized the crack grows along these.

So, it is a its a surface. The surface of the specimen, see that. You open this, you break open this, you look at the cracked plane, you will able to see the nice grains which are not elongated right. You can look at this, these are all grain, grains you see the grain facets ok.

You can see the clear grain facets, grain facets. The grain facets means the grains are not deformed, it like a sugar; the sugar grains, you see that right. So, they are not deformed. They are they are you know I mean the corrosion has occurred selectively along the grain boundary and the crack starts moving along the grain boundary.

So, the grain boundaries are relatively electrochemically active. I use the term electrochemically active. Because it can be an anodic can happen, you can even sometimes can even can have cathodic that happens in hydrogen embrittlement case. But so if the preferential dissolution takes place here and so, the grains are not deformed and you see a huge amount of a inter granular cracking taking place. This is one way of looking at it. There are cases where it is not necessarily 100 percent inter granular, 100 percent trans granular, it could be a mixed kind of failure, it can happen right. So, this is what really happens. In all these cases the failure is called as; I hope you heard of the term called Cleavage failure. What is the cleavage failure? Anybody has idea?

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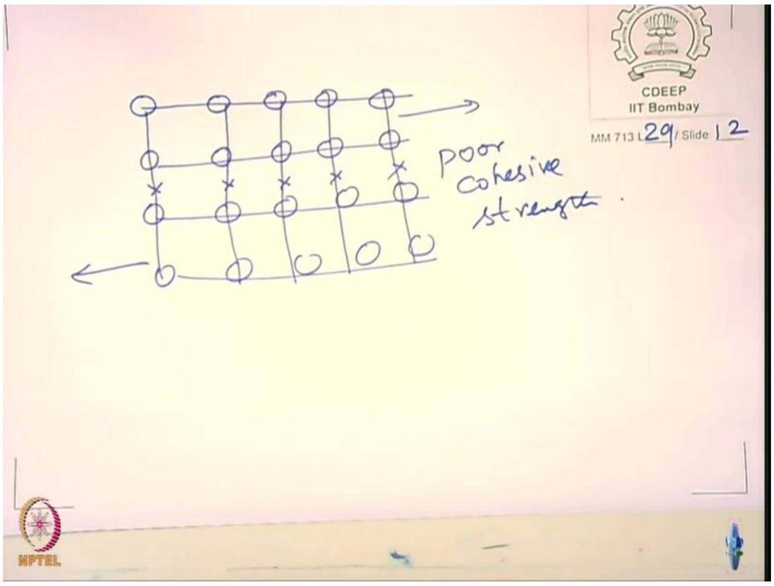

See lattice that I have right, when you apply force, the atoms start moving, when you have dislocations, you would no dislocation of course difficult for that to move. Now, when you when you pull it now assume that I use a scissor, I cut this bond, cut this bond, I cut this bond, I cut this bond, I cut this bond. If I cut this bond, what happens now? This piece becomes separate, this becomes a separate.

So that means, the atoms are intact, the positions are not changed because these are weakened now. So, the cleavage fracture means essentially the bond between the atoms are broken, well before the atoms could displace from their positions ok.

So, this is what we called in the cleavage fractures that what happened the grain boundaries, what happens? The atoms cleave right you have one grain another grain in between the atoms, there is just cleave out. It can happen that happens of course here in this case corrosion can lead to that happens. But you also have inter granular cracking taking place in air also right. You all you talk about temper embrittlement all these stuffs there ok.

So, so they are all cleavage fractures the atoms or you know the bonds between the atoms are I can say poor cohesive strength. It can happen and you can lead to this kind of failures. So, it is very important to understand the nature of cracking in a stress corrosion cracking failures; otherwise, you may get mislead. You may it consider that as what it could be you know normal tensile failures. So, cracking mode is a one of the one of the signatures of stress corrosion cracking.

Now, if you do not identify that, then you will not identify the problem you know. Let me just spend a minute and then, I will I think I will close this todays discussion. This one or you get a yeah, you if you find that a crack like this, the both of this are done what is called as you guys already studied sensitization right.

It is a stainless steel, they carried out ASTAM A262A test was done ok. You do not see any sensitization here. You see the sensitization taking place here right. Here also you have ASTAM A262A test right. But there are also sensitization taking place.

So, the alloy failed by brittle fracture in case 1 and the case 2; but the reason for failure are different right. The reason for failure in this case it is improperly solution annealed or improperly welded whatever kind of thing. Here everything looks ok, but the alloy is not good enough for the environment ok. So, the way you diagnose the problem is different. In this case, you say it is not the metallurgy is not adequate for the severity of the environment ok. You need to change the alloy.

Here, the primary cause seems to sensitization right. The sensitization is related to carbon content, welding, improper solution and treatment. So, many factors are going to be there. So, we need to understand how the cracking take place, before we can come to a conclusion what is the root cause of the problem in stress corrosion cracking. So, ah.

So, we have seen now the crack morphologies, the crack, the nature cracking and we will end our discussion today.