**Fracture, Fatigue and Failure of Materials**
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**Lecture No 29**
**Environment Assisted Fracture (Contd.)**

So, we have come to the 29th Lecture of this course Fracture, Fatigue and Failure of Materials and we are going to discuss some about the environment assisted fracture particularly focusing on the stress corrosion cracking as well as liquid metal embrittlement.

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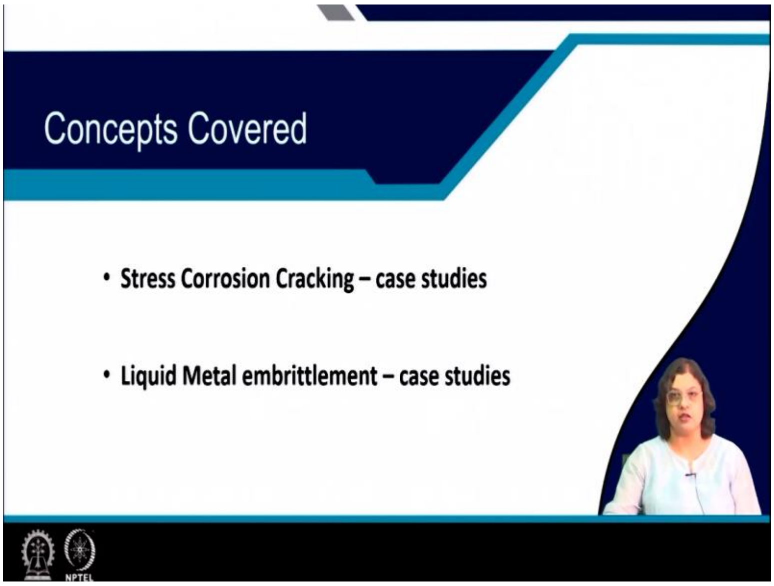


So, the concepts that will be covered in this lecture are the following. We will be discussing about the stress corrosion cracking with some case studies to understand what actually happens in case of stress corrosion cracking and how that can be avoided and then we will move on the liquid metal embrittlement procedures, mechanisms and we will discuss more on that.

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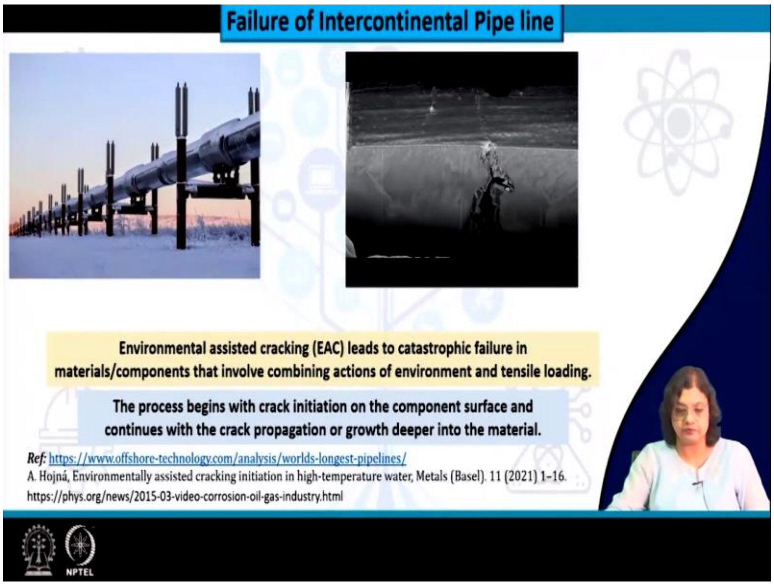


So, the picture that we are seeing here is the picture of an intercontinental pipeline which is used by the chemical and field industries to carry or transport the field from one of the countries or continents to another one and obviously it runs through several thousands of kilometers and passes through several different kind of atmosphere sometime extreme cold or heat or even in the marine atmosphere.

The material that needs to be used for making this pipeline has to sustain all such variation in the environment, but most importantly due to the presence of the external defect, for example, presence of the machining, marks or scratches on the surface that along with the presence of the internal or the residual stresses can lead to the onset of the stress corrosion cracking.

And that can lead to the overall total damage of the component of the entire pipeline as such. So, this has to be very well taken care of while designing this kind of pipelines and while employing this for certain number of years. So, it is necessary to have periodic inspection at the same time it is also not possible to have a very thorough inspection throughout these thousands of kilometers very vividly.

So, this needs to employ the proper designing concept based on the stress corrosion cracking failure mechanism. This video here shows that how the surface defect can lead to very easy or very fast growth of the crack and you can see that the cracks can develop at the multiple locations that can lead to the total catastrophic failure of the component.

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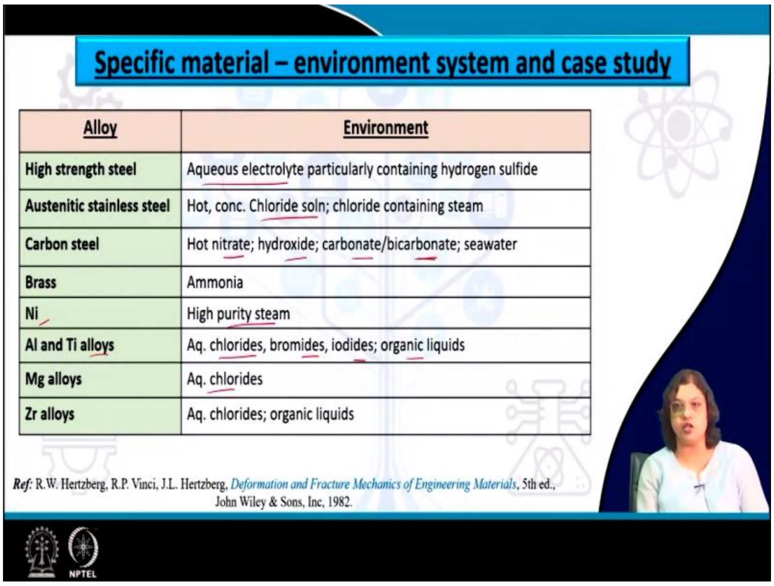


So, to understand that it is very important to have a general idea of what are the combination of material system and the environment that react with each other or that are more prone to undergo stress corrosion cracking. For example, high strength steel is very much prone to have reaction in presence of aqueous electrolytes particularly containing hydrogen sulphide. So, if we are planning to use a high strength steel for certain applications which calls for high amount of strength for the material.

We should be careful of not using it in presence of the hydrogen sulphide. On the other hand, if it is a steel, but of the austenitic stainless-steel category then the hot and concentrated chloride solution is very, very detrimental or even the chloride containing steam, steam which is already at high temperature is detrimental and that will lead to the reaction to occur faster and lead to the early failure of the component.

Carbon steel on the other hand is reacted to hot nitrate, hydroxide, carbonate, bicarbonate or even sea water. So, we should not use such kind of steel for applications which accounts for any such kind of components. Brass is very much reacted to ammonia. Now, this is very interesting and this has led to several incidence from which we understood the importance of separating brass and ammonia that this should not come in contact in any way that may lead to catastrophic failure.

I will just discuss about this in a minute. Nickel, for example, is reacted to high purity steam. So, just a moisture and higher temperature is enough to corrode nickel, aluminum and titanium alloys on the other hand both of this are expected to form the oxide the corrosive oxide layer and which are passive and that arrays the corrosion reaction up to certain extent, but the presence of aqueous chlorides, bromides, iodides or even organic liquids can act detrimental to this aluminum and titanium alloys.

Magnesium alloys on the other hand is reacted mostly to aqueous chloride. On the other hand, zirconium alloys are reacted to not only aqueous chlorides, but also any other organic liquids. So, while designing this kind of information one should have so that we can avoid the stress corrosion cracking to materialize.

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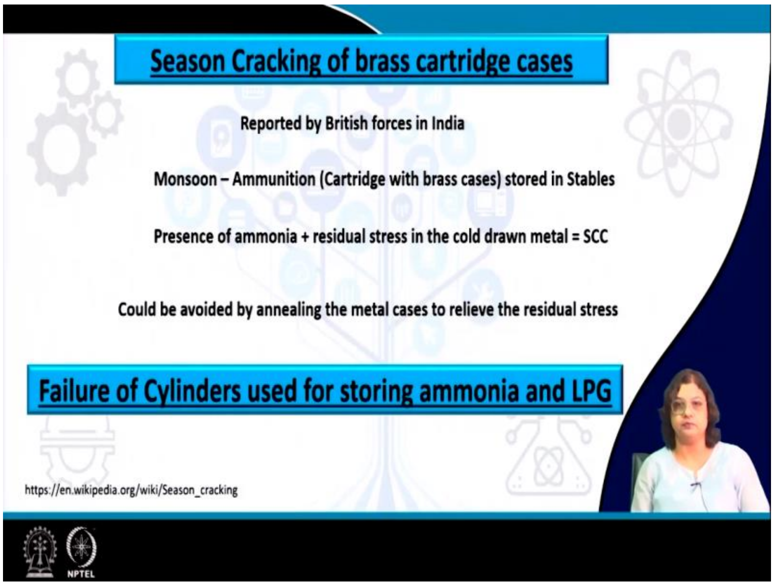


So, this is an incident known as season cracking which has happened in the dependent India which was under the British force at that time and this was reported by the military forces to the British government at that time that there was just cracking of the brass cartridge that is used like the cartridge that is used typically has a cover of brass. So, it just keeps on cracking on its own and that sometimes lead to some explosion also and could be quite catastrophic.

So, what actually has happened and what later on has been found out is that during the monsoon period or during the rainy season when there is no such use of those cartridge for the war they have been stored in the stable, stables for the horses. So, this cartridge typically has a brass case on the surrounding to protect it from the atmosphere or to make it stronger and what happens is that in this table during the monsoon with the moisture and the presence of ammonia particularly from the urine of those animals. This ammonia reacts with the brass casing of the cartridge. Now, you may ask that there is no stress because nobody is touching those things so nobody is applying any stress. What happens is that, this brass casing it has been made typically is made by cold drawing and during the process of cold drawing itself some residual stress is being stored in the casing itself.

And this residual stress clubbed with the presence of ammonia in this tables that leads to stress corrosion cracking of this brass casing. If the cracking occurs at a much faster rate and in an explosive manner that can lead to an explosion of the inner cartridge material as such and that can lead to quite catastrophic explosion as well. So, this however can be avoided if the casing had been annealed after cold drawing.

So that to relieve these internal stresses and then the presence of ammonia will react with brass and that will be detrimental for the brass casing itself like that will corrode the brass casing and that will damage the casing, but that will not lead to a catastrophic explosion or that will not lead to the crack growth. So, there will be just a corrosion, but not the stress part so that will avoid the fracture at least should not be catastrophic.

There was another such incident reported in USA where it has been found that there was a series of accidents that happened because the cylinders burst. Now, these cylinders this place of USA is mostly for the farmers. This has a farming land and the farmers used to stay there and they use the cylinders for their using this as the cooking gas as the LPG gas (liquid propane gas).

Now, the suppliers who supplies this gas they are also the supplier of the ammonia for the farming part as a fertilizer. So, they use the same cylinder for storing the ammonia and when it is not a farming season they use the same one for storing the LPG. Now, while transferring it for the usage of ammonia storing to the LPG storing what happens is that they do not clean it properly.

And there could be some amount of ammonia left in it which reacts with the brass parts of the cylinder particularly the fittings of the cylinder which are made of brass. So, this ammonia reacts with those brass and that corrodes it and in presence of the residual stresses particularly because it is used for storing the liquid gas. Obviously, there is stress inside and because of the presence of the stress had it been used for storing the ammonia that would have again simply corroded the brass fitting.

And that may lead to leakage of the ammonia that is it, but since it is used for storing the LPG which is at high pressure that leads to an catastrophic explosion and series of those kind of incidence happens and later on with the failure analysis people realize the importance of ammonia and its reaction with brass and realize the importance of stress corrosion cracking in general.

And it is also very important to know that, for example, in this case ammonia of the order of only one part per million is enough to corrode the brass. So, we have to very, very careful in using kind of combinations of material to avoid the stress corrosion cracking.

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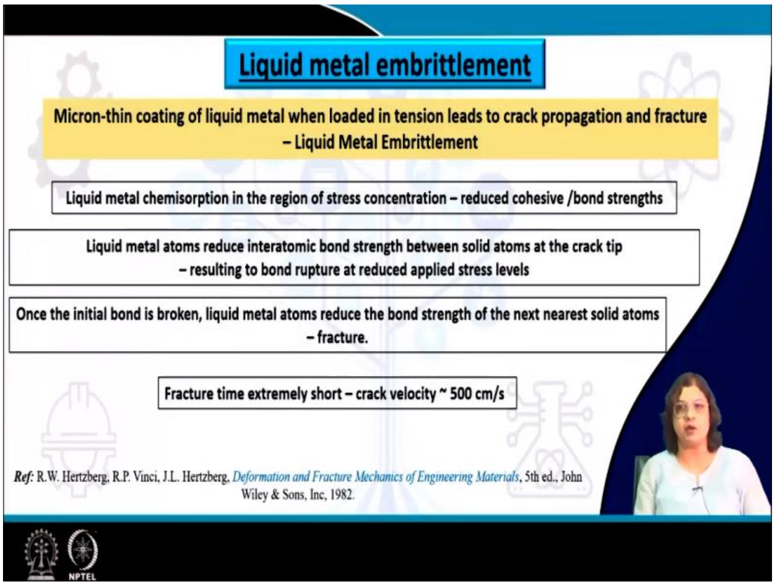


So, moving on to the next topic which is liquid metal embrittlement. What it says is that the micron thin coating of liquid metal when this is loaded in tension that leads to crack propagation and fracture that is what is a liquid metal embrittlement. So, we have one material over which there is a coating which is very, very thin of the order of few microns or even sub microns.

So, that coating of a liquid metal on that material leads to crack propagation and fracture. So, what could be the reason, how is this possible because here we are not talking of corrosion at the first instance. It is not like these two materials is corroding and then there is stress and that is why the principle that we have discussed for the stress corrosion cracking not exactly that, but what it is dependent on is the liquid metal.

Since it is in the liquid state it is being chemisorbed in the region of the stress concentration. So, wherever there is any defect or any cracks or notches or any corner or any such thing which is under stress concentration those sides are prone to have the liquid metal which enters there through the process of chemisorptions and that while it is inside the lattice it reduces the cohesive strength of the bond strength of the material.

And obviously the bond strength is being reduced that will lead to rupture of the bond. So, wherever this liquid metal atoms reduces interatomic bond strength wherever this happens at the crack tip it results to the bond rupture at reduced applied stress level in the vicinity of the crack tip. Now, once that happens it is kind of continuing the process itself it is like a chain reaction that once the initial bond is broken the liquid metal atoms reduce the bond strength of the next nearest solid atoms.

And finally, with this the crack extends till it achieves the critical value of the stress intensity factor that is required for fracture to occur and it leads to final fracture. Fracture time in this case is extremely short because the fracture, the crack propagates at a very high speed. The crack velocity is something like of the order of 500 centimeter per second. So, that is very, very fast and that means that if we have this liquid coating on some material then certainly that will lead to the liquid metal embrittlement in just a matter of few seconds or so very fast.

So, we have seen that hydrogen embrittlement is a kind of delayed process. So, there might be some kind of internal stresses which can remain unnoticed and then suddenly at the time of service even after years that can lead to fracture. So, that is one of the possibilities, one of the embrittling mechanism, the other one at the other end here is the liquid metal embrittlement when the fracture occurs very, very rapidly very fast.

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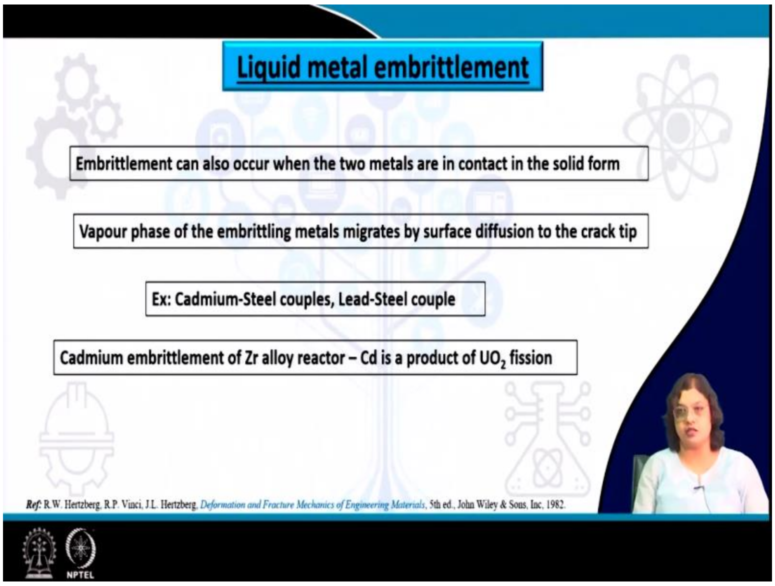


Now, liquid metal embrittlement can also occur when the two metals are in contact in the solid form. The vapor phase of this embrittling metals whichever is in the top which is forming this coating that migrates by surface diffusion to the crack tip or for that matter any other stress concentration side. Now, there are some examples that we should be concerned about. For example, the cadmium-steel couples or the lead-steel couple is a very, very reactive.

And this leads to this metal embrittlement where there are just two material that lead to the embrittlement and cadmium embrittlement in the zirconium alloy reactor that is also very well known one the cadmium here comes from the $UO_2$ fission. So, it is a product of the $UO_2$ (uranium oxide) fission reaction and this cadmium then reacts with the reactor material itself and leads to the breakage or leads to the failure.

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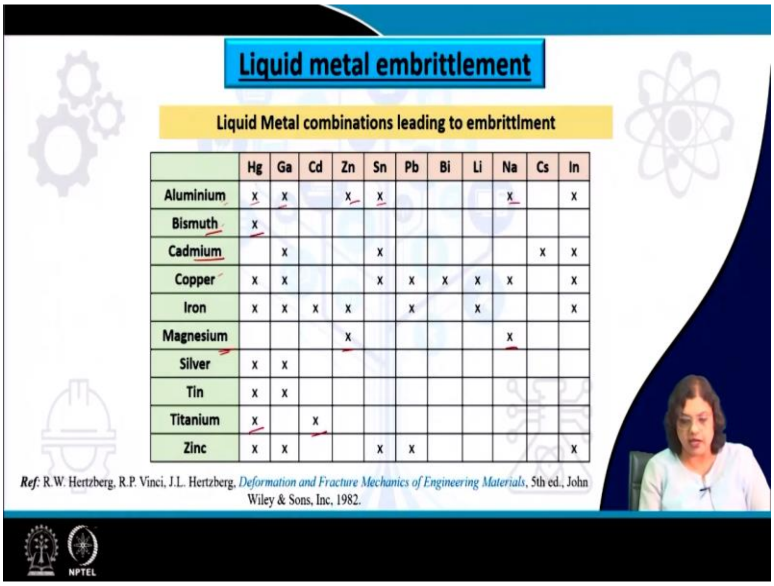


| | Hg | Ga | Cd | Zn | Sn | Pb | Bi | Li | Na | Cs | In |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium | x | x | | x | x | | | | x | | x |
| Bismuth | x | | | | | | | | | | |
| Cadmium | | x | | | x | | | | | x | x |
| Copper | x | x | | | x | x | x | x | x | | x |
| Iron | x | x | x | x | | x | | x | | | x |
| Magnesium | | | | x | | | | | x | | |
| Silver | x | x | | | | | | | | | |
| Tin | x | x | | | | | | | | | |
| Titanium | x | | x | | | | | | | | |
| Zinc | x | x | | | x | x | | | | | x |

So, here is the list of the metals which react with each other or that leads to embrittlement more than reaction that is actually what is happening that the liquid coating or the metal in the liquid film is getting either chemisorbed or getting surface diffused and lead to the embrittlement, reduces the bone strength and lead to the embrittlement. So, what we can see here is if we are looking at all the materials on the first column here we see that aluminum is being reacted to mercury, gallium, zinc, tin, sodium etcetera.

And we have also seen that amongst all the elements or all the metals on the first row itself mercury is the one which reacts with almost everything except cadmium. So, cadmium is the one which does not react with mercury and then magnesium is another one which does not react with mercury other than that all the metals such as aluminum, bismuth, copper, iron, even kind of noble metals like silver, tin, titanium, zinc everything reacts with mercury.

So, that is the most corrosive thing that we all know about that mercury is very, very that embrittles most of the metallic system. On the other hand, if we look for the metals which are less prone to undergo liquid metal embrittlement we should obviously talk about bismuth, bismuth reacts only with or bismuth gets embrittled only with mercury and not with anything else, but bismuth is also not readily used as a structural material.

So, if we are talking about structural material from the point of usage of fracture mechanics context then magnesium is the one which is also which mostly does not react with many of the metallic systems except for zinc and sodium. So, these two are the things which are very, very reacted to magnesium and lead to the cracking or embrittling. Titanium on the other hand is also very much resistant to corrosion particularly because of the oxide layer that it forms.

But in this case when we are not talking about corrosion, but rather than liquid metal embrittlement we see that other than mercury and cadmium, titanium is not being embrittled by any other metallic system. So, that can also be very safely used for most of the application.

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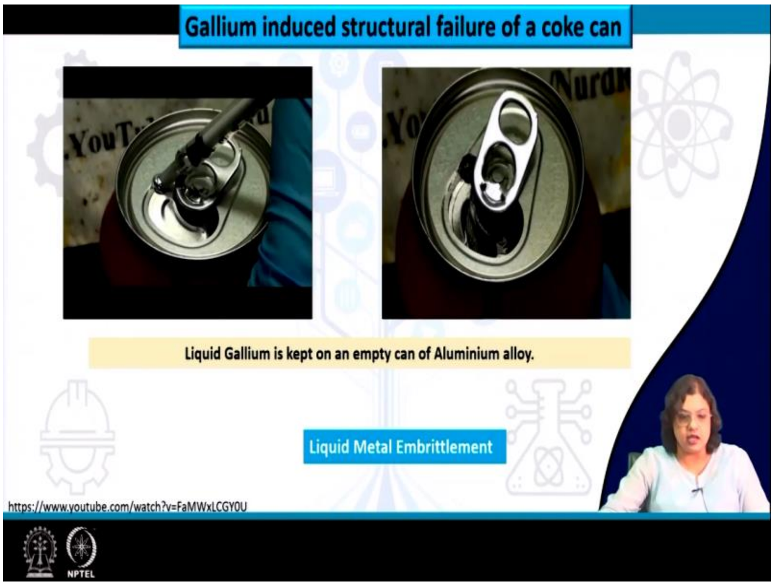


So, here is very practical example that I thought of demonstrating which shows how gallium will behave in presence of aluminum. So, liquid metal embrittlement concept for the combination of aluminum and gallium. Now, this is a coke cane made of aluminum we all know that these are the aluminum cans used for this kind of soft drinks and then here we see that piece of gallium in the liquid state is being put on this.

So, if we just spread the gallium to some extent what we see after sometime actually is something like this, it becomes almost like an embrittled one. It is fracturing very, very easily as if this is made of paper. We all know that how this soda cans it is very difficult to break it in this form like a paper and this happened only because the gallium has infiltrated in this aluminum and that lead to the embrittlement of the aluminum.

So, now that we know about the different ways by which environment assisted cracking typically occurs. We know about the hydrogen embrittlement or the stress corrosion cracking or the liquid metal embrittlement whatever it is the basic idea is that it fractures at a stress intensity factor which is lesser than the typical $K_{1C}$ value of the typical plane strain fracture toughness values of the material.

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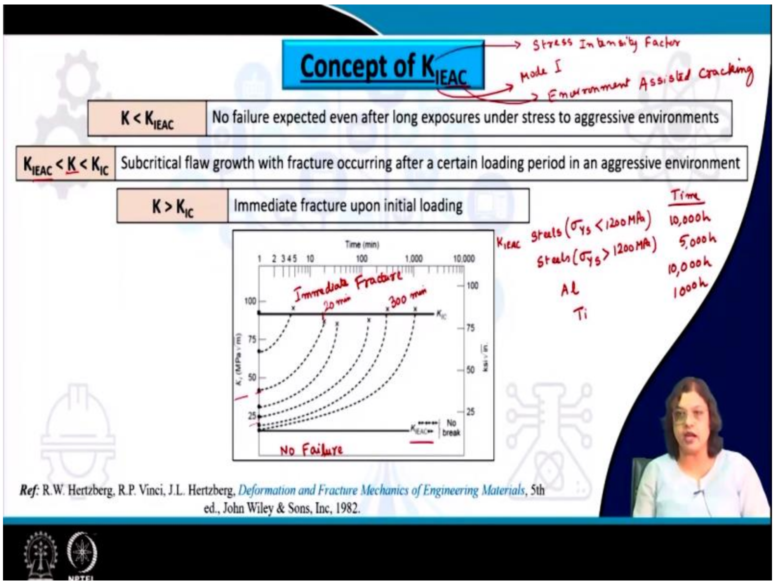


So, there comes the concept of $K_{1EAC}$ so the 1 here signifies mode 1 let me also write down the K here. So, K is nothing, but the stress intensity factor and EAC of course is environment assisted cracking. So, this signifies the critical value of the stress intensity factor at which material or component or a structure will fracture in presence of certain combination of environment or combination of different metals.

So, that means that if the applied stress intensity factor K if that is less than $K_{1EAC}$ then that means that there will be no failure. So, that means the level of the critical value of $K_1$ for the environment assisted cracking has not been reached and that means that no failure will occur even after long exposures under stress to aggressive environment. So, that is the safest mode when there will be no fracture at all.

On the other hand, if K is in between $K_{1C}$ and $K_{1EAC}$ so the value of K is greater than $K_{1EAC}$, but it is still less than the expected plane strain fracture toughness of the material. If we know the plane strain fracture toughness of the material from the lab scale and if we are employing this at a value of stress intensity factor which is lower than this $K_{1C}$ then it is not supposed to fracture.

But in case it exceeds the $K_{1EAC}$ value, then the subcritical flaw growth can occur with fracture occurring after the certain loading period. So, we need some amount of time for the reaction to materialize in an aggressive environment and that can lead to fracture. On the other hand, if the applied K is greater than $K_{1C}$ of course there will be immediate fracture whether there is environment or not, it does not matter.

There will be always fracture because it is exceeding the plane strain fracture toughness values of the material. Now, how do we find this $K_{1EAC}$? These values varies for different materials of course, but not only that even for the same material, even for the same specimen configuration if we are employing it for different amount of time $K_{1EAC}$ will be different. So, it is very difficult to standardize the method and rather we use this for different material we use a particular protocol to be used.

Now, how do we measure this $K_{1EAC}$ that will be different for not only different materials, but even for the same material if we are talking about the different aggressive medium or if We are talking about the same medium, but also the different amount of time that has been given to that material that can also influence the particular value of $K_{1EAC}$ even in the plane strain condition.

To understand that it is very important to use some particular standard method to perform the test. Of course, it is also at the same time very, very difficult to standardize this method because as I mentioned that it will be different for different materials, different conditions different time levels etcetera. So, what is typically being followed, particularly for metallic system it is just as an example.

When we are talking about steels which are of moderate strain for which the yield strength is less than 1,200 MPa for this we typically keep it inverse for 10,000 hours and perform the test to get the $K_{1EAC}$ value. In case we want to use steels for certain applications which are of high strain which is greater than 1,200 MPa, the yield strength is then we test it only for 5,000 dollars.

On the other hand, if you are talking about non-ferrous metallic system, for example, aluminum once again we employ the timing around 10,000 hours for titanium on the other hand we employed only for 1,000 hours. So, depending on the different kind of materials and the application we kind of select whatever time limit will be suitable and then only we can find out the $K_{1EAC}$ value.

So, this here shows some experimental results for $K_1$ of the $K_{initial}$ for the initial condition and the x axis here is the time. So, there are two limits the lower limit and the upper limit, the lower limit here signifies $K_{1EAC}$. So, if we are applying the K value less than this then there will be no failure at all. If we are applying the K value more than this $K_{1C}$ then there will be immediate fracture.

So, there is no doubt about that. Now, depending on the starting value of the crack and the starting K level that changes with time as we are increasing the starting value of K. So $K_i$ as we are changing as we are increasing the time that it survives to achieve up to the $K_{1C}$ level is also reducing, for example, if we are talking about $K_{initial}$ value of 25 MPa root meter we can see that it reaches the $K_{1C}$ for the same material till the time of something like around 300 minute.

On the other hand, if we are talking about the initial $K_1$ of 50 MPa root meter then it achieves this $K_{1C}$ more or less in something like 20 minutes only. So, obviously the initial value of $K_1$ is very, very important and we are sustaining this particular value for this much amount of time and we can see that it can survive for much lesser amount of time if the $K_1$ that is applied is higher. So, that is very important and based on this we can design on what kind of applications we require, what materials whether it will undergo any kind of embrittlement mechanism we have to be carefully understand and utilize that concept.

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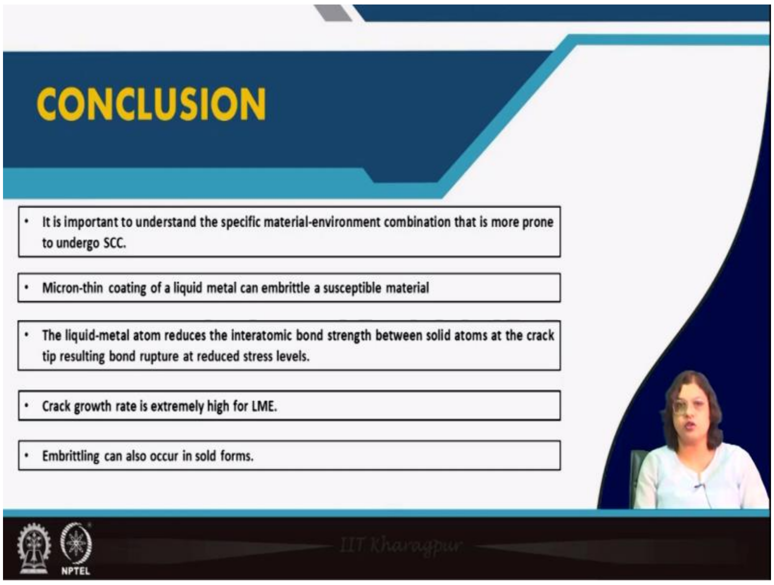


So, here are the conclusion for this lecture. It is important to understand as I mentioned the specific material environment combination that is more prone to undergo stress corrosion cracking in case we want to avoid that and for the case of liquid metal embrittlement what happens is this micron thin coating of the liquid metal that forms that material which is susceptible to undergo liquid metal embrittlement not every combination of metal will undergo liquid metal embrittlement, not every combination of material and environment will undergo stress corrosion cracking. So, we have to carefully use the particular material system.

Liquid metal atom in case of the liquid metal embrittlement that reduces the inter atomic bond strength between the solid atoms and this particularly happens at the crack tip and that results to bond rupture at produced stress level and what we have seen is that the crack growth rate is extremely high for the case of liquid metal embrittlement. Embrittlement can also however form in the case of the solid forms when the vaporization of one of the element or one of the metal can lead to the embrittling mechanism.

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So, following are the references that has been used for this lecture. Thank you very much.