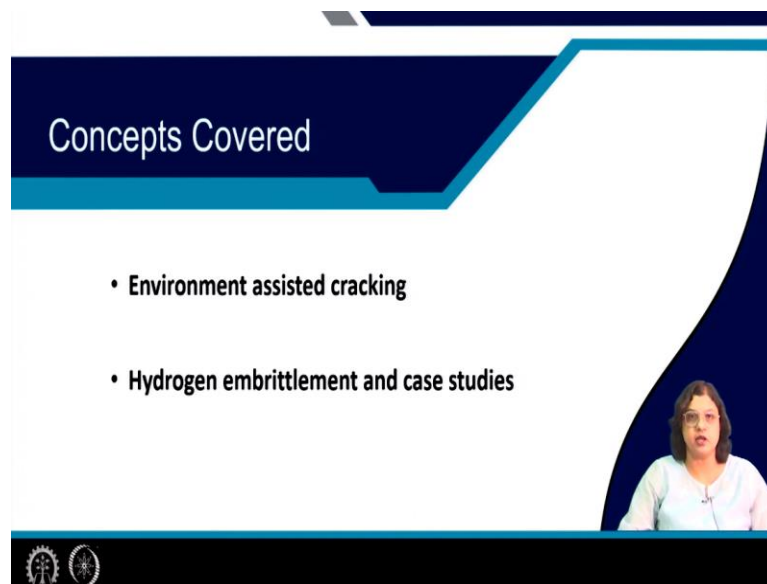


Fracture, Fatigue and Failure of Materials
Professor Indrani Sen
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Indian Institute of Technology – Kharagpur
Lecture No – 27
Environment Assisted Fracture

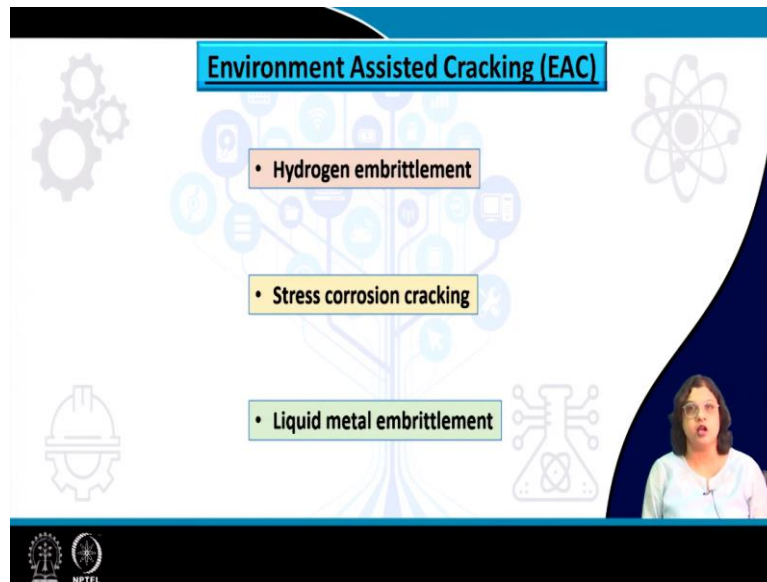
Hello everyone. We are in the 27th Lecture of this course Fracture, Fatigue and Failure of Materials and in this lecture we will be covering a very important topic on fracture mechanics which is the environment assisted fracture.

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The basic concepts that will be discussed in this lecture is the following, the different kind of environment assisted cracking and particularly we will be emphasizing on the hydrogen embrittlement and this would be explained with some case studies.

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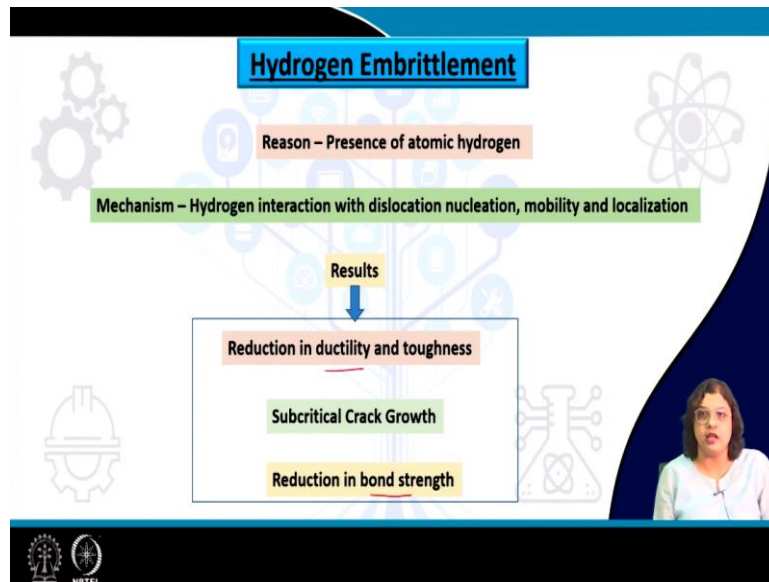


So, what happens in reality is that often we determine the plane strain fracture toughness of a material and then in actual practice it fails at a much lower values of the K_{IC} or the fracture toughness values are quite less than whatever is expected or whatever is determined from the lab scale testing. Now, this is particularly one of the reasons is the fracture behavior being aggravated by the environmental conditions.

So, there are typically three different kinds of environment assisted cracking which are of significance in fracture mechanics and we will be discussing about each one of them in the subsequent lectures. In today's lecture we will be particularly focusing on the hydrogen embrittlement as the name suggest that this is related to the presence of hydrogen in the environment and how is that affecting the overall fracture behavior of the component and mostly for the metallic system.

There is also another kind of environment assisted cracking which is called stress corrosion cracking. So, as the name suggests there is obviously presence of stress here and plus there are some affect of corrosion as well. So, both of this together can lead to an early onset of fracture which is dealt by the stress corrosion cracking and finally we will be also talking about the liquid metal embrittlement. So, there are some specific combinations of metals particularly which one of them in the liquid form actually embrittles the other. So, that will be discussed in the last section of this topic.

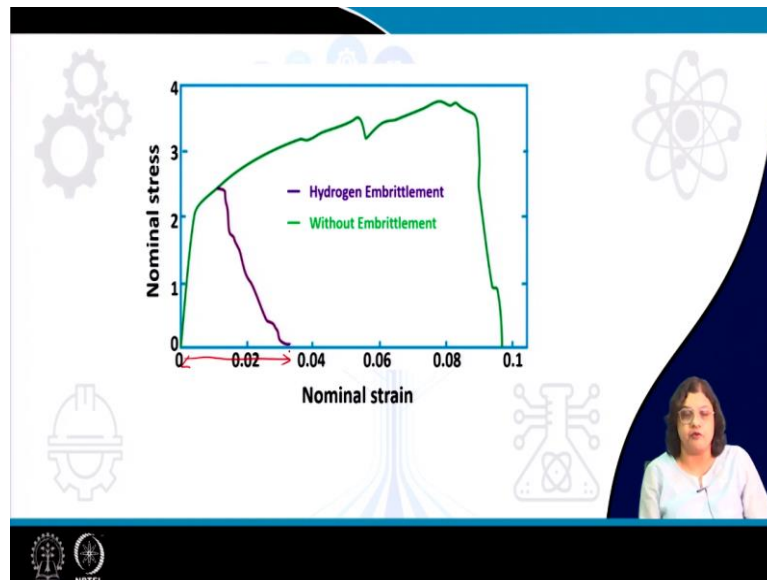
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So, let us move on to the first one; hydrogen embrittlement. As I mentioned or as the name suggests that hydrogen embrittlement is particularly related to the presence of atomic hydrogen and hydrogen in the atomic form is what is needed that leads to all the reactions to occur and that leads to the final failure. So, the mechanism more or less depends on the interaction of the hydrogen atom with the dislocations, the nucleation of the dislocation, mobility as well as localization process.

And that in turn results to the reduction in ductility and toughness and this is related to the formation of subcritical crack growth initially the crack is of smaller crack which then grows very, very rapidly and leads to the final fracture and this happens because of the reduction in the bond strength that makes the fracture process progress faster and that leads to the easy or the early onset of the crack.

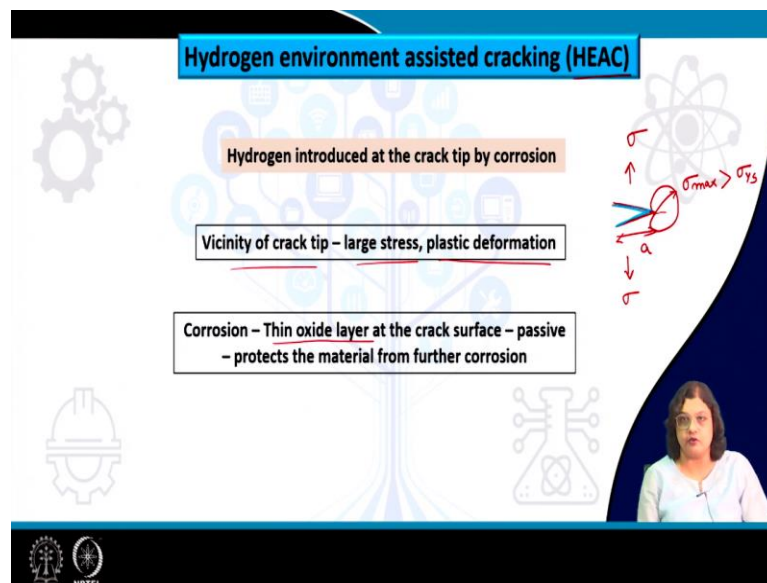
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As you can see so if we are considering the stress strain behavior of a material and the green one here signifies the experimental stress strain behavior of a material which shows quite a bit of ductility. On the other hand, because of the presence of hydrogen in the atmosphere and because of the hydrogen embrittlement to be active for the same material we see that the ductility has been reduced notably.

The purple one here signifies the stress strain curve in presence of hydrogen and obviously that is an alarming situation especially when we are talking about the components that are used for service in corrosive atmosphere or in presence of hydrogen we have to be really careful about this and for that we need to understand the basic reasons for the hydrogen embrittlement, the basic mechanisms and of course how we can avoid that.

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So, there are different ways by which this hydrogen embrittlement occurs. One of this is the hydrogen environment assisted cracking or HEAC. So, this signifies that hydrogen is introduced at the crack tip by the process of corrosion. So, this hydrogen comes as the corrosion product and at the vicinity of the crack tip because of the presence of large stress there is of course some plastic deformation that happens.

We are already familiar with the deformation ahead of a crack tip we know that if we are applying a stress to a component which is having a crack let us say of length a at the tip of the crack the stress is maximized by the factor stress concentration factor and in case this σ_{max} exceeds the yield strength of the material we know there will be plastic deformation that occurs.

Now, plastic deformation is nothing, but the formation and the movement of the dislocations. So, this along with the corrosive medium will have an interaction and that will lead to the further growth of the crack. In fact, because of the corrosion reaction there is thin oxide layer that forms at the crack surface. So, all this surface we see that the corrosive layer forms. So, let us say these blue layers here is the corrosive layer particularly or mostly oxide layers.

And this in most of the cases is a passive one which signifies that this layer of the corrosion product the blue layer one here protects the material from further corrosion. So, that in some sense acts beneficially until at some point it ruptures and lead to the final failure. So, we will come to that. Before that let us see that how the presence of a crack and the presence of a corrosive environment how does that actually work?

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Hydrogen environment assisted cracking (HEAC)

Hydrogen embrittlement

Looses metallic ions close to the crack tip – crack tip behave as anode

Away from the crack tip – Passive layer behave as cathode

Excess electron on the anode - pass through the conducting body – to the cathode

Evolution of Hydrogen gas – Hydrogen diffuses to the component

Grain boundaries are more anodic – tensile stresses at the vicinity of crack tip – hydrogen atoms being small in size – diffuse to grain boundaries, defects, voids, inclusions etc.

In fact, the metallic ions which are close to the crack tip that is being lost and that serves as the anode. So, the crack tip itself serve as the anode. As you can see here that because of this plastic deformation here this protective layer gets ruptured and that lose some metallic ions making it a anode. On the other hand, the other part the wake of the crack particularly which is covered with this corrosion product layer that serves as the cathode layer.

And the corrosive medium whatever it is that serve as the electrolyte. So, overall this entire system acts as an electrolytic set where we have this cathode and anode and electrolyte and all the regular electrochemical reactions occur. One thing I would also like to clarify here that when we are talking about the environment assisted cracking it is very important to understand that this is more or less an interdisciplinary subject.

So, we need to have a solid understanding of not only the mechanical behavior or metallurgy, but also, we need to understand the physical metallurgy as well as the electrochemistry, surface chemistry so all those kind of things we have to have a solid understanding and then only we can correlate the behavior of each of this factors and how they are being controlled.

How they are affecting the overall corrosion behavior as well as the fracture behavior. So, as you can see here because of the presence of the electrolytic or simply the corrosive medium which serves as an electrolyte we get an entire electrolytic cell here having the cathode and the anode and the electrolyte all together. Obviously, there will be the chemical reactions which we will be acting and as a result this excess electron which are forming on the anode pass through the conducting body.

So, the body or the component acts as the conducting body here and these electrons will pass through the cathode and in this process the hydrogen gas is being evolved. This hydrogen actually diffuses to the component, hydrogen the size being very small it is also quite easy to diffuse the hydrogen inside the system or inside the component. So, that in some sense act as the source of hydrogen in this case particularly this hydrogen diffuses to the different locations.

Grain boundaries are typically more anodic and the tensile stresses at the vicinity of the crack tip that is also a site which is prone to undergo the corrosion reaction because there is already some existing stresses present there and hydrogen atoms being small they diffuse to this location. So, the grains boundaries to the defects, voids, inclusions or any such locations hydrogen tends to diffuse to such locations and accumulate. So, this is overall the way hydrogen embrittlement works.

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Internal hydrogen assisted cracking (IHAC)

Presence of dissolved hydrogen in molten metal

Hydrogen Flaking: Dissolved Hydrogen in the molten metal forms entrapped gas pockets upon solidification

Localized stress associated with the gas pockets generates sharp cracks

Spalling of steel

A flake (dark circle) due to excessive hydrogen which contributed to the fracture of a turbine rotor in Arizona (Yukawa et al. 1969)

NPTEL

There are another way other than the environmental hydrogen there are the internal hydrogen that also can lead to the embrittling of the component which is known as internal hydrogen assisted cracking. So, this signifies the presence of dissolved hydrogen in the molten metal or hydrogen is already existing in the system and one of the significance or one of the very commonly found defects or hydrogen embrittling defect is hydrogen flaking.

So, this signifies that the dissolved hydrogen in the molten metal, so while the metal is still in the molten state the hydrogen which is already dissolved in the system that is entrapped in the gas pocket. So, there are various gas pockets when it is being cooled in a regular atmosphere and on that the hydrogen is getting entrapped upon solidification. So, this is I am able to get out of the systems gets trapped in this gas pockets.

So, obviously the side effect of this would be that there will be some localized stresses or internal stresses that will be generated because those gas pockets are filled with the hydrogen and it being lighter will always have a tendency to come out however the entire system is now a solid one upon cooling. So, of course it is not able to get out obviously that will turn on having the internal pressure or the residual stress also.

And because of this overtime that generates the sharp crack. You can see here flake which is something like this a circular one which is very clearly visible here pretty big one and that is due to the excessive hydrogen which contributed to the fracture of the turbine rotor. So, you can see that such a big flake can form and if we are doing the proper failure analysis of the fractured surface we can understand that this is because of the formation of the flaking.

And which might have been because of the presence of the hydrogen which gets entrapped in the gas pockets. So, if we do all this postmortem analysis we can figure out the actual reason for the cracking to occur and that finally; so, if have this flaking that basically leads to spalling of the steel. So, that is how it breaks down and we have the entire components fractures in a brittle manner. So, that is what makes the hydrogen embrittlement very, very difficult situation and we tend to avoid that.

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Flake dia ~ 3 cm

$a = 1.5 \times 10^{-2} \text{ m}$

$\sigma_{\text{app}} \sim 350 \text{ MPa}$

$K = Y\sigma\sqrt{\pi a}$

$K_{1C} = 34 - 59 \text{ MPa}\sqrt{\text{m}}$

$K_{1C} = Y_1 Y_2 \sigma_F \sqrt{\pi a_c} \rightarrow 1.5 \times 10^{-2}$

\downarrow

\downarrow 350

\downarrow 1

\downarrow $\frac{2}{\pi}$

A flake (dark circle) due to excessive hydrogen which contributed to the fracture of a turbine rotor in Arizona (Yukawa et al. 1969)

Now, here is a simple example and exercise for you to do what we have seen there is the flake dia is something like 3 centimeter. The applied stress at the point of fracture is 350 MPa and we know from the given literature that the K_{1C} value the fracture toughness lies within this range of 34 to 59 $\text{MPa}\sqrt{\text{m}}$. So, if such kind of failure occurs and if we are doing the failure analysis or we need to understand the reason for this failure we can simply look into the fracture surface to figure out the actual reason.

For example, in this case considering this flake which has already been formed and which is having a very nice circular shape having a diameter of 3 cm which means that if we are considering this as the entire defect size a in this case will be something like $1.5 \times 10^{-2} \text{ m}$ if we are considering this as the defect and that lead to the fracture.

σ is already given here what I intend here is to find out the K case the stress intensity factor that is required for fracture and we can do this if we are employing the relations that we have understood if we are using the typical relation as K is given by σ or $Y\sigma\sqrt{\pi a}$ and in this case considering a circular defect what we have is $Y_1 Y_2 \sigma\sqrt{\pi a}$.

At the point of fracture of course this will be K_{1C} and σ will be σ_F a will be a_c . Of course, it has fractured at this point so this a_c is nothing, but $1.5 \times 10^{-2} \text{ m}$ Y_1 considering that this is a central crack or void or this flake. So, we can consider Y_1 having the value of 1 Y_2 on the other hand has the value of $2/\pi$ considering that this is a circular void.

And σ_F is already given here this is at the point of fracture of 350 MPa and a_c is as I mentioned it is 1.5×10^{-2} . So, if we do that we should be able to find out the value of K_{IC} which if you can do this exercise yourself you will find that this follows well within the limit of this one. So, that means that although we are applying a stress value of 350 MPa which might not have reached such a high value of K_{IC} because of the presence of this hydrogen flaking here we can reach this value of K_{IC} . At least locally and that will ensure the fracture to occur. So, that makes it very, very important to find a way to avoid such kind of flake formation at the first place.

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<https://weldingengineers.co.nz/news/weld-defect/cold-cracking-low-hydrogen>

Internal hydrogen assisted cracking (IHAC)

Presence of dissolved hydrogen in molten metal

Breakdown of residual water/organic compounds during welding

Diffusion in the weld plate while the weld is hot

Embrittlement occurs after cooling due to hydrogen trapped in the weld (creates internal stress) and heat affected zone (martensite with brittle microstructure)

Hydrogen induced cracking/cold cracking - delayed phenomenon
- occurs after weeks/months after welding

5mm

Now, let us see what are the other mechanisms of this internal hydrogen assisted cracking. As I mentioned that IHAC is considering that the hydrogen is already dissolved in the molten metal and this can also happen by the breakdown of the residual water or if there is some organic compounds during the welding that may breakdown and that lead to the presence of the hydrogen.

So, this diffusion in the weld plate while the weld is hot. Diffusion of hydrogen into the systems already hydrogen is there while the weld is hot. Now, when it turns cold when the plate is being cooled down at that point this hydrogen once again is trapped in the weld and that creates the internal stress. Now along with that if we are cooling this particularly the cooling rate is very, very high.

So, that means that the metal typically considering here as an iron or steel-based alloy we know that because of the faster cooling rate that forms the martensite. Now, martensite once

again is a very, very brittle structure. Martensite has a high hardness, but very less ductility or toughness. So, martensite is a brittle structure. Now, after cooling what happens is that the hydrogen is entrapped in this weld.

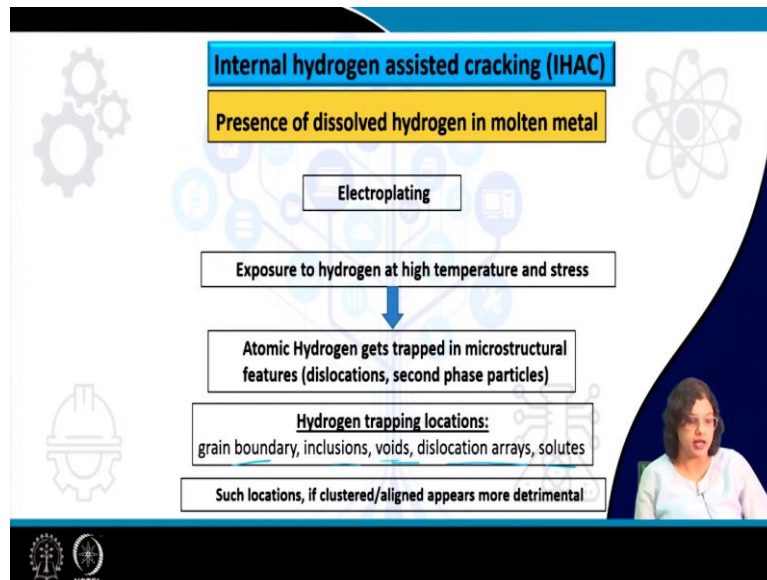
So, that creates an internal pressure plus the presence of the martensite. This internal pressure leads to the formation of micro cracks or tiny cracks there in the system and that along with the presence of the brittle martensite phases lead to the overall cracking of the system. So, that is known as hydrogen induced cracking or more commonly this is known as cold cracking.

As the name suggests this happens while the component is already in service. So, this welding operations has been employed on the component at the time of manufacturing or fabricating the component and now while everything externally looks good while this is in service after a certain number of times or sometimes months, weeks or sometimes even years there this failure happens just like that without any prior intimation.

So, this is basically very, very delayed phenomena that the hydrogen has been entrapped and that the hydrogen is creating the internal stresses and because of the presence of martensite that is forming the micro cracks that is growing to the final fracture this everything remains unnoticed because this is happening internally and particularly this is happening in the cold condition like in the regular condition.

So, that makes it very, very difficult and dangerous and it needs to be always avoided. So, cold cracking is a phenomena through which even component which is in service for many years suddenly one fine morning breakdown and we have to be very careful of not having this embrittling system at the very first place.

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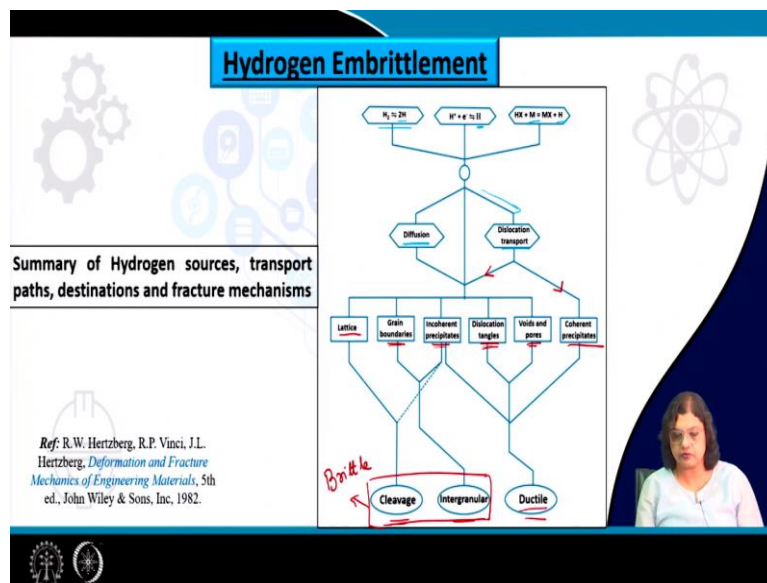


Hydrogen can also come from the electroplating. Now, this is an irony since electroplating is mostly used to have the material higher corrosion resistance, but that itself can insert or include the hydrogen in the system or in some cases if the component if we know that this is in service in the hydrogen atmosphere in presence of high temperature and stress so that also lets the hydrogen to enter into the system that high temperature and stress facilitates the hydrogen to enter into the system.

And then this atomic hydrogen gets trapped in the microstructure feature. So, any kind of defects as I mentioned the dislocations or second phase particles, voids even the grain boundaries all these locations are prone to entrap or absorb the hydrogen and that leads to the creation of the internal pressure. These are the common hydrogen trapping locations like the grain boundaries, inclusions, voids, dislocations, arrays sometimes even the solutes also which leads to the hydrogen entrapment and final failure.

Now, if such locations are randomly oriented or randomly distributed that is still okay, but in case such trapping locations particularly voids or inclusions if they are clustered at some locations. So, that means that there are many such voids and that means that the high-volume percent of hydrogen will be entrapped there or in case that this defect is trapping locations are aligned along certain orientations in case those orientations are perpendicular to the loading directions certainly that will lead to very early easy onset of crack. And that will lead to the final failure. So, those are very, very detrimental in case such trapping locations are clustered or aligned along certain directions.

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So, this is the hydrogen embrittlement in short. So, it shows the summary of the hydrogen sources so let us see what could be the sources that we have discussed. So, either there are this gaseous hydrogen which is dissociated into the atomic hydrogen or there are this hydrogen ion which again forms this atomic hydrogen because of some reactions or the corrosion reaction.

We can also have this chemical reaction with the hydrogen chloride or sulfide along with the metal that will also release the atomic hydrogen. Now, once this hydrogen is there inside the system this needs to be transported. So, that is the second state for hydrogen embrittlement to occur and this can happen in two different ways either through diffusion. So, when the hydrogen can enter into the system or this is being diffused to the actual lattice or the different parts of the components or this can be transport through the dislocations.

So, this can happen so the presence of dislocation which can act as a career for the hydrogen atoms. Now, if the hydrogen is being diffused or by transported by dislocations they end up into the different parts of the components. So, let us see where it goes when it comes to diffusion. So, when the hydrogen is being diffused it may come to the lattice the crystal lattice so that is the most internal space for the hydrogen can be or other most probably sites for the hydrogen to get entrapped is the grain boundaries or with the presence of precipitates particularly the incoherent precipitates or the dislocation tangles.

So, if there are many dislocations which are tangled or piled up those are also the locations where the hydrogen can get trapped as well as the in the voids and pores. So, we have already

seen that these are the probable sites on which hydrogen gets located and these are the places where the hydrogen can come if it is coming through the diffusion. Now, dislocation transport if the hydrogen is being transported through the dislocation and they can go to all these places through this path here.

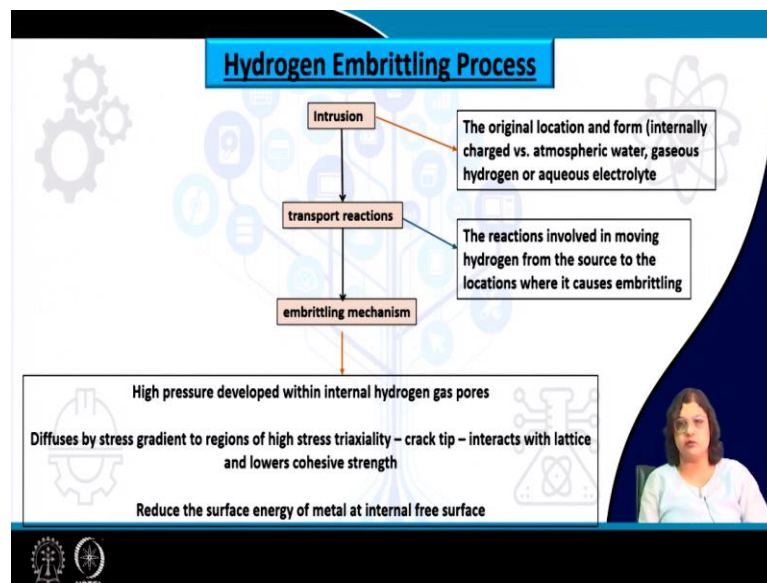
So, basically it can go to all these places as the lattice and the grain boundaries and the incoherent precipitates, dislocation tangles as well as the voids and pores, but what extra it can do is it can also go to the coherent precipitates. So, both kind of precipitates can accommodate the hydrogen in case it is being transported through the dislocation that will be easier for the hydrogen to find its next place.

And now based on the position of the hydrogen in any of this defect side we can also figure out that what kind of fracture mode it will have, for example, if it is in the lattice obviously there will be cleavage kind of fracture because it is moving on to the lattice and when it breaks it forms a facet. So, it forms the cleavage kind of fracture. If it is in the grain boundary then it is more prone to form the intergranular fracture.

And while coming to the incoherent precipitate that can lead to either the intergranular fracture or that can also have the ductile kind of fracture depending on the position of this incoherent precipitates as such. If the hydrogen is present at the dislocation tangles or even the voids and the pores it should have the ductile kind of failure and even when present in the coherent precipitates would still have a ductile kind of failure.

So, that means that if component or a system has under grown hydrogen embrittlement from the fracture surface we can see all different kinds of fracture. It could have the signatures of ductile fracture or it could have the signatures of brittle fracture, this cleavage as well as the intergranular one both of this signifies as the fracture mode being brittle as well as if it forms a typical ductile fracture. Well, it is present in the coherent precipitates or in the dislocation tangles, voids etcetera. So, by looking on the fracture surface it is difficult that what is the exact mechanism, but what we can at least inform or we can understand is that where the hydrogen might have come from.

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So, based on this let us just summarize this embrittling process. So, first of all hydrogen needs to be included in the system and this is related to the original location and form particularly whether it is internally charged or it has come from the atmospheric water or gaseous hydrogen or aqueous electrolyte this dictates that how the hydrogen will form and how the hydrogen will include in the system.

So, that will also have its effect on the next process which says that the reaction involved in moving the hydrogen from the source to the location. So, that is ensured by the transport reaction, how the hydrogen is being transported, so what is the carrier whether it is going there through diffusion or through the dislocations that will dictate where it will end up and finally the embrittling mechanism can be summarized as follows.

So, there is a high pressure developed within the internal hydrogen field gas pores and because of this pressures that diffuses by the stress gradient to the regions of high stress triaxiality typically crack tip as we are all aware, the crack tip is having high stress triaxiality so that is a location hydrogen is prone to get accumulated and once it does that actually the next step that it serves is lowering the cohesive strength of the lattice itself.

So, once the hydrogen is trapped at any locations other than developing the internal stresses or having these residual stresses it also acts in lowering the cohesive strength of the lattice and that leads to reduction in the surface energy of the metal at those internal free surfaces and that leads to the hydrogen embrittling process, the entire system get embrittled and fracture at a much lower applied stress.

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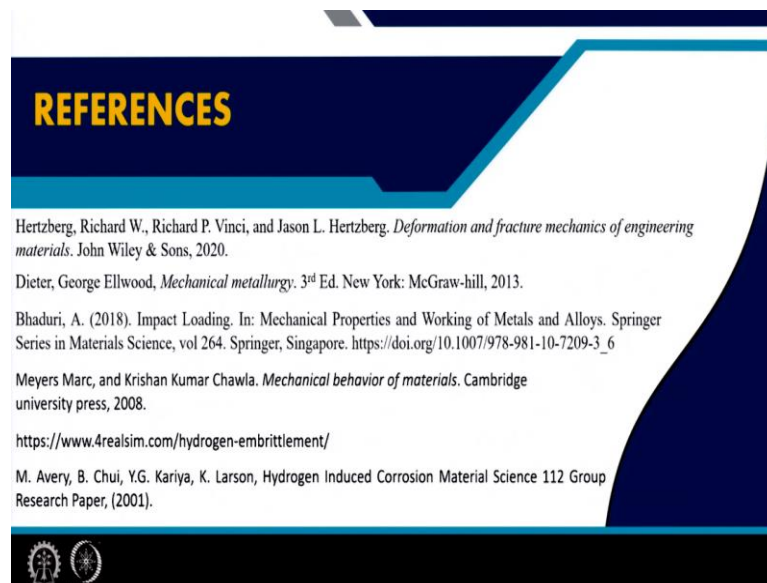
- Hydrogen embrittlement is related to the generation of internal stresses and reduction in the bond strength of a metal or alloy due to the presence of atomic hydrogen.
- Molecular hydrogen is dissociated by chemical adsorption on iron, which causes liberated atomic hydrogen to diffuse internally and embrittle the metal.
- Hydrogen tends to accumulate at grain boundaries, inclusions, voids, dislocation arrays, and solute atoms.
- Flaking and Cold cracking are commonly seen hydrogen embrittling effects.

So, let us conclude this lecture here with the following points that hydrogen embrittlement is related to the reduction in bond strength of a metal or alloy due to the presence of atomic hydrogen and this occurs by several steps. First of all, the molecular hydrogen is disassociated by either chemical absorption on iron or there could be some corrosion reaction as well that causes the liberated atomic hydrogen to diffuse internally.

And that leads to embrittle the entire system. Hydrogen tends to accumulate particularly at the grain boundaries, inclusion, voids, dislocations, arrays and solute atoms and we have seen that how the accumulation of hydrogen leads to presence of the internal stresses and that leads to generation of micro cracks which finally develop a crack that is sufficient to break the entire system or fracture the entire system.

And that leads to hydrogen embrittlement along with that this also causes to reduce the bond strength of the lattice and that also results in embrittling the system and flaking and cold cracking are the two very important phenomena that we have seen which are the commonly seen effects of hydrogen embrittlement and should be always avoided.

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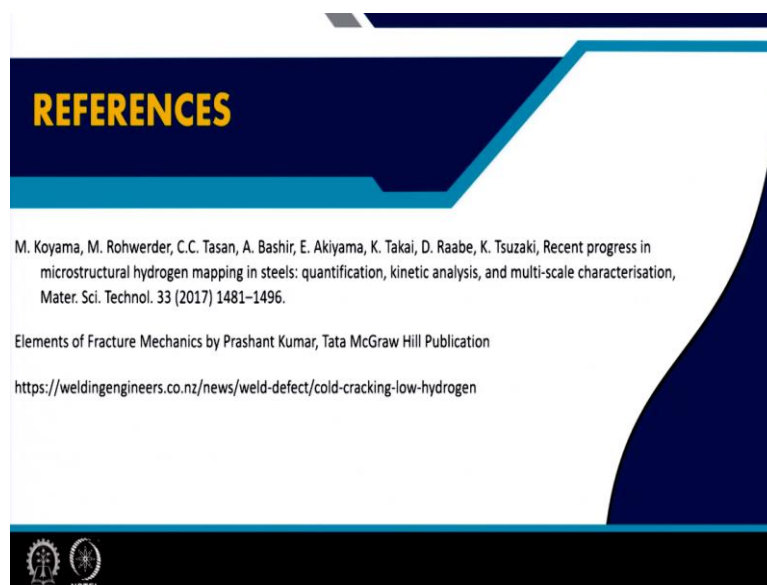

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Following are the references that has been used for this lecture. Thank you very much.