# **Aqueous Corrosion and its Control Prof. V. S. Raja Department of Metallurgical Engineering and Materials Science Indian Institute of Technology, Bombay**

# **Lecture - 32 Forms of corrosion: Hydrogen damage**

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The next topic of interest for us is what is called as the Hydrogen damage. This is a very interesting and important subject, somewhat similar to stress corrosion cracking; but the mechanism of cracking is different. I have used the term broadly as hydrogen damage as given by the Fontana book. In all these cases, the main species for responsible for premature failure is hydrogen, but the way the hydrogen causes the failure is different and so, we call broadly as the hydrogen damage.

Under this, we could have Hydrogen Blistering are also called as Step wise cracking; the other one is Hydrogen Embrittlement; some people loosely term it as hydrogen induced cracking, we call Decarburization; the fourth is Hydrogen attack. I would like to say that 1 and 2 are ambient temperatures processes and 3 and 4 are high temperature failures.

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You see look at that again briefly not going much into details; let us now discuss the topic of hydrogen blistering.

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So, typical failure you know happened in one of the refineries and located in Mumbai. You can see how the sample bulge; we call a blistering. Primarily, because the hydrogen accumulated in somewhere here and created the pressure and so it happened. If you look at microscopic level you see that this, these are all stepwise zigzag kind of cracks and to look at even more at a microscopic level, they are micro cracks ok; it happened ok. And this is actually a cross section of a pressure vessel. So, we will discuss this in detail, why does it really happen and how do you prevent the hydrogen blistering of steels.

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The hydrogen blistering generally occurs in low strength steel. Let us look at the mechanism, how the hydrogen can cause problem. We all of us know that you know hydrogen is the tiniest element in the periodic table ok. This, I do not think there is any other element which is smaller than that and hydrogen in the atomic form can diffuse through the metals and steel for sure, you can diffuse through that.

They can diffuse through the interstitials and so, it can cause two types of problems; the one type of problem is hydrogen blistering. Let us take a cross section of steel here, steel plate or a vessel, it is exposed to say an acid, make it simple. Exposed to an acid and this is steel iron, the steel has got a small defect and this defect is it is a pore.

When the metal corrodes, what is the reaction you get? You have iron going as Fe 2 plus plus 2 electrons and H plus can combine with electron to form atomic hydrogen right. These are all we know. These things happen at the surface and hydrogen ions move towards the surface and accept electron and form hydrogen atoms. All these are all adsorbed hydrogen. Please notice that these are all atomic hydrogen, they adsorb on the surface. The following things are possible; 1, H plus. None no.

H the hydrogen atom can combine with the other hydrogen atom and it can form a hydrogen molecule and it can escape from the surface, that is they can simply combine and go out escape as hydrogen. The second chance is that the hydrogen diffuses through the metal. For example, it can diffuse (Refer Time: 08:40) out as hydrogen here. It can diffuse can (Refer Time: 08:45) out as hydrogen here. Here they can combine and the hydrogen gas can get liberated. It can happen in many of the cases.

In fact, in some pipeline corrosion monitoring, they monitor the amount of hydrogen that is escaping the pipeline and related to the corrosion rate, you know is not it? Each iron that is getting oxidized one atom, you have one gas molecule is getting released right. You have 2 electrons and 2 electrons in a combined with H plus and form one gaseous hydrogen molecule.

So, by monitoring the amount of hydrogen, you can monitor the corrosion rate; in fact, people do that. So, you have this option taking place. The other option is through the metal and escape. Third option is hydrogen diffuses and get trapped at the internal defects and become hydrogen molecule right.

So, you will have quite a bit of in these places, you can have hydrogen molecules. It can build up pressure. In the case of 3, hydrogen builds pressure, advances the crack. So, what is the role of hydrogen? The hydrogen role of hydrogen is just to exert pressure; the existing defects, they grow that is what they do that in which case the fracture here is a really a ductile fracture, you are not going to get any brittle fractures. The hydrogen does not interact in with the lattice at all.

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Now, the fracture here is ductile, the strength of the steel also less only. Steel quality also unclean steel. So, in addition to the pores and cracks, you can also have other trap sites. Especially, you can have manganese sulfide stringers and especially, you have it in killed steels, when rolled. When you roll it, the manganese sulfides they elongate, they stretch and if you see this in the micro in the microscope, you will see they are all in the planar these are all in the planes; manganese sulfide inclusions.

Now, what happens in this case? The hydrogen get accumulated here; hydrogen accumulate and cause micro cracks right. So, what happens then? The micro cracks coalese requires and form larger cracks. So, for example, you know this, this can grow, this can grow, this can grow and then, the join and the form stepwise cracking; finally, leading to blister.

Please see that these cracks generally grow parallel to the surface. They grow parallel to the surface. Why? All these stringers are aligned in a plane and that plane is parallel to the surface of may be pipeline or maybe a pressure vessel.

So, it is a material problem. First of all, it is a material problem. The material has is not clean; in the sense, it has got pores and micro cracks, the steel has got inclusions and they especially the manganese sulfide stringers are there actually.

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Poisoning of the Interface<br>Memme, hydrogen is less allowed<br>I contine and escape as note and. Mems, hydrogen is less around to combine and escape as more one<br>If the summare of the steel has MM 713 32/ Slide 05 to combine on the street man<br>If the surface of the system of opents  $S$ , As, Sb, P: Porsoning<br>
Retard Yecombination reaction  $H + H \longrightarrow H_2 \longrightarrow Teta$ <br> $H_1 + H \longrightarrow H_2 \longrightarrow Teta$ Retard Yearner Hz = the Person of Hz = the Mns = pood trap soites<br>Mns = pood trap soites<br>Mns = pipelines: Crude may have Hz S gas.<br>Crude oil pipelines: Crude may have Hz S gas.

Now, what are the factors that affect this more? Poisoning of the interface; what is mean by poisoning? Here, the sense when say poisoning here, it means hydrogen is less allowed to combine and escape as molecule. If the surface for example, if surface of the steel has sulfur, arsenic, antimony and phosphorus; all these are all poisoning agent. These are all poisoning agents right.

Though they; so they hold the hydrogen on the surface for quite some time, they do not allowed. That means, the actual they retard recombination reaction. What is the recombination reaction? Hydrogen plus hydrogen giving rise to molecule, this is retarded.

When this is retarded, what happens? They have enough time for the hydrogen to get into the steel and in the steel, the manganese sulfide inclusions; there are two problems here. The good trap; is not it? The good trap sites because the sulfur they trap the two manganese sulfide is a long stringer. What happens to the steel? It is toughness, is transverse ductility is less.

So, that is the kind of problem that you have. So, it is a problem of surface. Now, these elements like arsenic, antimony, sulfur, all can come from the environment right. Now, if you are going to have crude, if you say crude oil pipeline, crude oil pipelines may have and you know in this crude may have hydrogen sulfide gas. This is called as a sour gas.

So, crude may have some sour no. So, sour gases right and this hydrogen sulfide acts as a poison and so, there are problems. There are all problems in the oil and gas industries, the transport crude oil and crude oil in many cases, it has a hydrogen sulfide gas and so cause the problems and sometime, these cracks can be it can be few foot length.

It can happen, it is not small; it can have a very long cracks ok. So, we have seen this mechanism, how do you control this?

Student: (Refer Time: 20:11).

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Contain<br>O Lower H2S in the environment<br>O Cleans steel<br>3 Enibitars 114713132 Slide 06

Yes, first of all lower  $H_2S$  or poisoning elements in the environment. This may not be possible always right, it depends upon the crude you are going to get; you can reduce of course, then they also use de sulfides and all they do that. But that is not going to be you know easy in all cases. Go for a clean steel.

You can also go for inhibitors. Please notice, if is no corrosion, no hydrogen; so, no hydrogen blistering. You can control the corrosion and 4 can talk about the coatings.

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Idrogen Embrittlement tydrogen Embrittlement<br>Occursin high strength steels. Scansm<sup>10</sup><br>Fracture is brittle. CDEEP<br>IIT Bombi Fracture is brittle.<br>O de cohesion (HEDE)<br>O de cohesion (Hedropen enfrom MM 713 L 32 Slide 07 HELP, hydrogen enhonced localised<br>HELP, hydrogen enhonced localised HELP, hydrogen enhanced<br>Lowers the sinyace energy. 3) Lowers the Surface<br>Decalasion: Lowers bord strength: Lowers in Lowers bord strength<br>Decalasion: Lowers bord strength<br>HELP Assist the dislocation motion.<br>HELP Assist the dislocation  $H = LP$  Assist the dustine Mg,<br>Hydride formation:  $Ti$ ,  $Er$ , Mg, LP -> Assuration: Ti, Zr, Mg,<br>Hydnide formation: Ti, Zr, Mg,<br>Hydnides are brittle:<br>AIDE, Adsorption Induced dislocation Emission.

Coatings eliminate the corrosion and so, hydrogen blistering becomes very less. Hydrogen embrittlement, it occurs in high strength steels; high strength steels and the fracture is brittle. There are quite a few mechanisms here in this ok. There are quite a few mechanisms and I just name it and then, move on and because this is this is very involved subject. One is decohesion; another is HELP called as hydrogen enhanced localized plasticity. There was also some model which talks about. It lowers the surface energy.

You know what do you mean by lower surface energy? You when you create a when you fracture it, you create a new surface. This energy required to create a new surface. When hydrogen gets adsorbed, then what happens? Then, the energy required to create a new surface reduces. It is a simple mechanical model.

In the decohesion, you know the decohesion comes with the, it lowers the bond strengths. It lowers the bond strength and so, what happens? You can cleave right, the energy required to cleave the atoms, they become less. So, that is called as hydrogen induced decohesion model, they call it HEDE; they call it ok. This also called as HEDE, hydrogen enhanced decohesion model and HELP means what happens? It lowers, it assists the dislocation motion.

The dislocation can move even at a stress level lower than the yield strength. Assume that the dislocations moves below the yield strength, there will be no ductility; localized plasticity right and so, it becomes brittle.

So, anyway I given you a broad, I mean contours about the mechanisms of this. There is one more mechanism is also talks about hydride formation. These things are happening in the case of titanium, zirconium, even magnesium and you know some of these materials, they form hydrides and hydrides are brittle. So, when they are brittle it you know it refracts us you lose the ductility of this.

There is also anyway there is also one more model called as AIDE, Adsorption Induced Dislocation Emission actually model. So, there are a lot of things you know the aide mechanism is basically of course, that way even AIDE, HELP and HEDE are all crystallographic models actually right, all involving the dislocations and as well as the cohesion in the lattice.

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It will be nice to compare stress corrosion cracking versus the hydrogen embrittlement. Stress corrosion cracking, again I am very simplifying it; I am simplifying it. Stress corrosion cracking is anodic dissolution involved. In hydrogen embrittlement, what is involved? Hydrogen evolves, there may be metal dissolution, there may not be hydrogen dissolution, there may not be metal dissolution right.

So, either that can be metal dissolution; most cases, it can happen because hydrogen evolution how it can come unless metal dissolves, it gives electrons, H plus cannot reduce to hydrogen ok. But it is not necessarily it can happen. I can do a cathodic protection and iron evolution can occur ok. So, this is anodic dissolution. Here, this is a hydrogen evolution process are occurring.

So, if you look at the Fontana book and this give a nice distinction between these two. So, potential and this axis is time to fail. How long it takes the time to fail? If I apply a negative potential in relation to the  $E_{corr}$  if the time to fail it decreases like this, this is the time to failure right. For every time is time to failure. So, it is the fail here, this is no fail and I also have a similar thing here fail, it is no fail.

Can you now guess or just to analyze what you call such failure and what you call this type of failure? What would happen? Suppose, if it fails faster right, this is it is a time axis right. When I increase the potential positive, the time to failure decreases; it becomes faster. So, what you call this failure, if I can classify as SCC and hydrogen embrittlement, what do you call this? Choose between these two.

Student: Still (Refer Time: 30:30) hydrogen embrittlement.

So, this is your hydrogen embrittlement failure and this is going to be SCC. So, one way to differentiate is whether the metal undergoes hydrogen embrittlement or SCC's to apply a potential. If we apply a positive potential, if the metal does not fail, then you say that it is what? It is prone to hydrogen embrittlement, may be prone to hydrogen embrittlement.

If you apply a negative potential, it does not fail and it fails in the positive side; then, you could not say that it is susceptible to SCC. Why? When you do a cathodic polarization, what is happening to metal, what is happening here? Here, what happens now? Over here, metal dissolution decreases right, metal dissolution decreases, metal dissolution increases.

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So, you can able to understand why things really are happening at all. There is one more way of distinguishing these two. I thought I will just discuss that too. I have not discussed to you the strain rate all the stuffs and the ductility. Strain rate is let us say it is 10 power, it is a minus 8. I just give something. It is a 10 power minus 1 something like that ok. Here I carry out a simple tensile test right.

The specimen is immersed in the environment of interest, when I carry out a tensor stress, tensile test, I pull the sample at a given strain rate. What is the strain rate? How do you define a strain rate? What is strain delta l upon l right and strain rate means again is going to be your time d t. So, it is going to be your strain rate; this is going to be your strain rate.

So, what rate at which you are going to pull in relation to the of course, it also involves the gauge length right; l is the gauge length and delta l is elongation extension and of course, dt is a time ok. The metal can behave like this; two types of behavior, the metal can exhibit. The first one, how does it behave the ductility is very high at high strain rate; also, high at low strain rate.

Another one the ductility gradually decreases and then, almost becomes steady state now actually. It does not take off again ok. How do you explain this? If you want, I can say that the case 1, one corresponds to stress corrosion cracking. The two corresponds to hydrogen embrittlement. Now, let us discuss ok. Why I would assign the one, the curve one to SCC; whereas, the second curve, I have assigned it to hydrogen embrittlement. Well, let us let us look at SCC.



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What is SCC, we discussed earlier? At least in the slip assisted dissolution model right, what did we discuss there? Ok. One I can have case 3. It is not a well-drawn, a smooth curve suppose I draw it like this ok. Now, you tell me, the order of susceptibility of material 1, material 2, material 3, I get it like this and this is scratch or when slip step forms, the current increases and then, decreases same manner. You tell me what will be the order of increasing susceptibility to stress corrosion cracking?

What will be the order of increasing susceptibility to stress corrosion cracking? We are talking about a model which is slip assisted active dissolution model for stress corrosion cracking. Use that model. Now, you tell me which one you would expect to be the highest susceptible and lowest susceptible?

Student: Sir, the 3 will be the lowest I think, then followed by 1 and 2.

3 will be the?

Student: Least.

Lowest least that is right.

Student: And 1.

Then, 1; then become 2 right. You are right. Why are why you saying like this?

Student: Because re passivation time (Refer Time: 37:20).

So, the time for re passivation. So, the Q, you talk about Q ok. The Q if you see here ok. Q 3 is the lowest, then you have Q 1, then becomes Q 2. So, time for re passivation becomes a factor. So, that is the key issue.

Now, there are two things happening; one you are deforming, the film is broken, other is the re passivation right. Now, let us look at this curve now. If you pull the sample so fast, the time for the dissolution is very less. Because I when I pulled very fast, how long it takes to fraction the sample? It takes less time to fraction the samples.

So, you are going to get a purely a mechanical failure. The time the sample resides in the environment during the completion of the test is very low here because the time taken to fracture is very less because of the high strain rate. So, I do not expose to environment for long time. So, it becomes totally ductile, I understand this.

So, when you are allowing more time for exposure as the strain rate is lowering, then what happen? It becomes a maximum here, this also you can understand here. Why does it go back? It goes back because before the mechanical you know, before the mechanical you know stress breaks the film, the film is again reforming. So, you do not have.

So, there are two process opposing processes; one is the film breakdown, other is a re passivation. The film break down occurs because of the mechanical strain right. So, if the strain is so low ok, the film is not really broken that much. It is able to re passivate compared to the film breakdown.

So, in this case, it is easy to heal; it is easy to heal the film and so, the time. So, the ductility becomes more and so, you get more elongation here. In this case of course, you have a bare metal, it time taken for exposure is so low. Here is optimum.

So, you are going to get the highest SCC susceptibility in this case taking place. So, that is why it goes through a bell curve and have the lowest ductility over here in SCC. Hydrogen embrittlement is a different story together right; how does the hydrogen embrittlement work?.

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 $\sigma$ H needs to differse and reach the crack CDEEP Di filusion  $IITB$ mhay MM 713 L 32 Slide  $\overline{1}$ raising strain can reach faster  $H_{\infty}$ thom the crack advo mechanical straining Can attist Crack soonts  $\sigma$ 

The hydrogen embrittlement works SCC or hydrogen embrittlement, it works differently right. Assume that I have tensile sample and I apply a load here, tensile load. The crack starts advancing now. We are given different models in a de cohesion model or localized plasticity model, AIDE model, whatever model it is going to be there. In all the models, I need hydrogen to act if hydrogen is not there; then, it is not going to act that means, I need hydrogen at the crack tip ok.

So, the hydrogen now what happens start diffusing to the crack, diffusive to a crack tip here ok. The hydrogen diffuses to the crack tip. So, hydrogen needs to diffuse and reach crack tip. So, the diffusivity of hydrogen is very important diffusion coefficient is very important.

Now, whatever be the diffusion coefficient ok, the two factors that would advance the crack; one is the rising strain, strain rate, the crack advances when you apply a strain rate; other one is the diffusion of hydrogen right. If hydrogen can reach faster, then the crack advancement right by mechanical straining, then the what it can do? It can now it can assist the crack growth right.

So, when the crack front I have hydrogen it assists, if it is not there; it is going to mechanical failure. So, it depends upon the diffusion rate. Now, look at this; if I am going to now lower the strain rate, the concentration of hydrogen at the crack tip will be increasing if I lower the strain rate right. Is not it?

If I pull it very slowly, then what happens? The diffusion rate is same almost, you do not worry about the strain induced diffusion at all. Forget about that assuming that diffusion coefficient is constant and if I strain it very slow like this, then there will be ample hydrogen on the crack tip and so, the cracking occurs right.

So, now look at this now, look at this plot, go back to this plot here. As I lower the strain rate, you expect more and more hydrogen to crack these the crack tip and so, the effect becomes more. It becomes steady state because after that it saturates, it does not really go beyond that level.

So, it becomes saturated. So, the hydrogen embrittlement tendency increases when you lower the strain rate and lowers only one way; whereas, SCC, SCC you know this stress corrosion cracking goes through a bell shaped curve and you have an optimum value of strained rate that gives you the maximum SCC and this optimum value will depend upon the alloy.

You know it may have the same for all the alloys, it could be different for stainless steels for and it could be different for aluminum alloys, magnesium alloys and so on so forth.

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So, you have seen the hydrogen embrittlement behavior of the metal and and what causes the embrittlement. You can say one thing that if the strength of the strength of a an alloy increases, the strength of alloy increases, the hydrogen embrittlement tendency also increases which means if I take a steel of let us say 1000 mega Pascal, the critical amount of hydrogen required to form a crack, if it is called some x value, if I increase the strength level to 24 hundred mega Pascal for example, ultra high strength steels.

Then, it could be much less than that it can be even 1 PPM level of that. For mild steel, you can even have 20 PPM or 100 PPM nothing happens. So, as the strength level increases for a steel, the tendency of the steel towards hydrogen susceptibility increases more and more and you have fracture mechanics concept, we will not enter into why does it really happen.

It is enough to say that the retardness become less when the strength of the metal, it increases. It can happen in aluminum alloys, it can happen in steels, it can happen in other metals as well. So, this is one thing that we should be aware of that. So, the hydrogen embrittlement, I would say can be a function of strength and the concentration of hydrogen.

Of course, one more called as applied stress. Please notice, if you do not have, you do not apply a stress. no cracking occurs here. In the previous case, in the hydrogen blistering the cracking occurred without any external stress; here, you need to have an external stress. So, you need to note that the difference right. So, external stress is required for hydrogen embrittlement to occur, blistering not required.

Similarly, here you get a brittle fracture; whereas, in the case of hydrogen blistering, it was a ductile fracture this happens in high strength steel; whereas, there it happens in the low strength steels and unclean steels.

So, you please see the difference between ok, you want to call it as a brittle fracture, this is your hydrogen embrittlement; hydrogen bristling, it is a ductile fracture. 2, applied stress needed; no applied stress needed. Generally, in high strength steel; happens in the low strength steels and both of them of course, are ambient temperature fracture process. What creates hydrogen in the system?

You know there are what are the sources of hydrogen, the hydrogen source, it could be you know corrosion simply a corrosion process. It can lead to hydrogen; 2, electro deposition could be cathodic protection right. It could be maybe during welding and welding case, what happens? You have using a in humid conditions right; humid conditions, it can be in steel making process.

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Hydrogen Embrittement is a vertersible<br>process:<br>Degas H, then ductility can be recovered MM 713 L 3 2+6lide  $|3$  $H_1$  $t_{2}$  $6ap$  $250$  $+$ asplated time

Several places the hydrogen can be a source. Fortunately, hydrogen embrittlement is a reversible process. So, if you can degas hydrogen, then ductility can be recovered. So, people have studied you know some work on this time to failure versus the applied load on this and they have done it on a steel which was coated by electro deposition process. You know when you do electro deposition process, you make the metal into a cathode and hydrogen evolves and part of hydrogen gets into the material right.

So, you find that the behavior goes something like this. This is as plated, it is baked to say baked now; t 1, t 2, t 3 and t 4 right. What is t 1? They are all baking time t 1, t 2, t 3, t 4, the baking time. Normally, if it is a steel you can have in the range of 180 degree Celsius to 250 degree Celsius. If you do it and most of the hydrogen can get escaped, some hydrogens can still remain as a trapped hydrogen that may not of course significantly affect the hydrogen embrittlement.

Please notice the hydrogen embrittlement occurs only if the hydrogen is diffusible because the hydrogen does not diffuse, then embrittlement does not occur. Why? It has to go to the crack front.

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Contal 1 Reduce the 4 level. 12 Reduce the Final stresses 2 Reduce the applied struss. MM 713 32 Slide 14 Reduce Corrosion. Reduce Connession.<br>Reduce stress concentration. 10<sup>-6</sup>cm/5 blainc<br>Ferritic streel = prove to HE 10<sup>-12-7</sup>15 Reduce stress<br>Ferritic steel = prove to HE 10<sup>-12-27</sup>15<br>austenite steel = restistent to HE 10<sup>-12-2</sup>715

Control; how do you control this? First of all, reduce the hydrogen level in the material right. 2, what you can do? Reduce residual stresses same thing, what you do for SCC right. Of course, reduce the applied stress ok, you coating all this and reduce corrosion.

When I reduce corrosion hydrogen intake reduces reduced stress concentration, there are several factors you can also look at reduce stress concentrations in the structures wherever you have. But very interestingly, if you take; if you take a ferritic steel and austenitic steel, it could be steel or stainless steel. This is resistant to hydrogen embrittlement prone to hydrogen embrittlement.

What is the reason? Anybody? Because the diffusion coefficient for hydrogen, they are all changing quite significantly right. It can be 10 power minus 6 centimeter per second. It is a plain carbon steel and it is 10 power minus 12 centimeter; actually you know diffusion coefficient comes in centimeter square right per second right.

So, you can see about 10 power 6 times you know the diffusion coefficient is less for austenitic stainless steel. So, austenite's are generally more resistance to stress corrosion crack; sorry more resistance to hydrogen embrittlement than ferritic stainless steels which is the contrary true. Ferritic stainless steels are more resistance to SCC and austenitic stainless steels are more prone to SCC. So, we need to understand the basic reasons why these materials behave in that way.

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Decarburization Decouburization<br>Steel -> major strength comes from<br>C:<br>Steel  $\frac{17200}{1700}$  -<br>Steel  $\frac{17200}{1700}$  - 1700 + CH4. Fe(c)  $\theta$ <br>Fe(c)  $4H \rightarrow$  Fe + CH4 Fe comments.<br>Surface Surface contrides<br>H Santace outformes intention steel, form CH4 gas

So, continuing our discussion on hydrogen damage, the third type of hydrogen damage is decarburization. You know the steel, if you take steel, the major strength comes from where? It is coming from the carbon right; from carbon. Now, if you are talk about a steel at ambient temperature, the solubility of carbon in the ferrite is very low right. So, the solubility of carbon is very low.

So, what form the carbon present in a steel typically, that leads to strength. If you take a microstructure of a carbon steel, what kind of microstructure do you see. You will see a ferrite and what else you see? You will see a pearlite right, the pearlite consists of ferrite plus the cementite.

Now, this combination gives the higher strength the cementite. In fact, gives the higher strength to steel. Now, suppose so you have essentially alpha plus pearlite and the pearlite is nothing but alpha plus Fe3C right. Now, suppose I take this steel and I subject it to a temperature ok, a temperature greater than 200 degree Celsius and I have hydrogen in this system.

Now, what would happen? That steel is nothing but iron and the carbon is present. The carbon is present as a pearlite. When you do this, when you heat steel and in hydrogen, now what is suspect would happen?

Student: Plus the hydrogen.

So, when this steel is exposed to hydrogen atmosphere, the temperature about 200 degree Celsius right, then what can happen now? The carbon present in the steel will react with hydrogen and it can form a methane gas. So, the carbon is essentially removed right. When you do this, then it becomes what? It becomes an iron and it becomes a methane gas. Now, this reaction can.

Student: CH 4.

CH 4. This is a 4 hydrogen here, you can balance the equation.

Student: Top one.

Sorry. You are right; thank you. So, it is a methane gas is CH4. So, the carbon can interact with the hydrogen either in the atomic form or in the molecular form. If it is in the molecular form, it reacts only the surface. Then, what happens? It removes the surface carbides right.

You have a carbide essentially you have this. Now, with the atomic hydrogen diffuses into the steel and then, form methane gas and this can happen. Now, what happens? The molecular hydrogen of course, the atomic hydrogen also can react with the carbides present on the surface is possible right.

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Diffusion of c to surface<br>depth of corbide free 3one A MM 713 L 3 2 6 lide 16 CH4 build pressure -> Intergranular

Now, what could really happen right? If we look at the reaction, essentially it is a diffusion of carbon right; diffusion of carbon to the surface, when you remove carbides because the concentration of carbon at the surface is reduced because of decarburization. So, the pearlite in the bulk will slowly decompose into iron and the carbon will migrate to the surface and then, form surface methane gas ok.

So, you see this happening. So, over a time period what happens? You see the carbide now the depth, depth of carbide free zone increases with the time right. As the time passes more and more carbides will decompose and come to the surface and form the methane gas.

It is also possible the atomic hydrogen, the hydrogen can also migrate inside and can form a methane gas in the grain boundaries. These are all methane gas and they build pressure. If you build pressure in the grain boundaries, what will happen to the grain boundary? Deform the form intergranular cracking.

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I show you the micrographs of a steel containing 0.1 carbon because you have some chromium, you have some molybdenum, you have some vanadium in this. Without exposure to the high temperature and hydrogen content, you can see the microstructure here; you see a nice pearlite quite large extent of pearlite is seen right. On exposure to hydrogen, now holding in for about what is more than 110,000 hours, you can see that the amount of pearlite got reduced because of the decarburization happening within the steel.

So, this is one of the problems happen in industries; especially, it happens in hydrocarbon industries, wherein you do what is called as catalytic cracking of hydrocarbons right. If you crack, so you get a indent gas right; you get a indent gas. How do you get indent gas? You get indent gas from long chain hydrocarbons, they are essentially liquid right and you fragment into smaller molecules, they become gas and then, they compress and give you as a liquid.

So, when you take a long chain hydrocarbon, you crack them into fine smaller molecules, you what happens now? You see that the hydrogen also evolves along with that. So, there is a free hydrogen, the catalytic cracking is done at high temperatures because of the generation of hydrogen, these steels they suffer decarburization. Now, decarburization leads to two kind of problems; one of course, is the cracking as I mentioned before, the other thing that can happen is can you fill up that what can happen, if you remove carbon?

Student: Strength.

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Strength falls down. Contan this CDEEP Form stable conbides Form stable continues<br>Alloy the street with Cr, MM 713 L 3 2 Slide 18  $Fe(C) + H_2 \xrightarrow{D} Fe + CH_4$ Partial pressure of  $H<sub>2</sub>$ Nelson Curres  $Z$ cr- $\frac{1}{2}$ Mo.  $1cr-\frac{1}{2}Mo$ T steel  $P H_2$ 

Strength falls down. So, this is a severe problem over here. So, how do we really control? How do we how can you really control; how do you control this? You need carbides to form you know I mean to have high strength to impart high strength to steel right. They are required, but the carbides interact with hydrogen they decompose. So, how do I minimize decarburization? Any strategy? So, you have to form stable carbides right. You have to form, what is called as the stable carbides. You have some idea about stable carbides, you know iron carbide is not that stable.

Can you tell me an alternative carbide which is more stable than iron carbide? It could be titanium carbide could be vanadium carbide, it could be as simple as chromium carbides. You know very well you know when you dealt with sensitization of stainless steels chromium carbides form in preference to iron carbide because that is the most stable phase as compared to iron carbide.

So, you alloy the steel with chromium, molybdenum more specially and you can also add vanadium kind of stuffs vanadium, you can have titanium all this kind of compounds; but more importantly, people add chromium and molybdenum to that. Now, look at this equation temperature right. Now, the decarburization tendency depends on what? Can you look at this equation and tell me?

Student: Presence of hydrogen and temperature.

It is the presence of hydrogen and temperature. So, what how do you quantify this? It depends upon the?

Student: Partial pressure.

Partial pressure of hydrogen and the temperature of the reaction. So, people have generated some data on this. Temperature, partial pressure of hydrogen, this is the simple carbon steel. This is 1 chromium half moly steel and also have 2 chromium of moly steel. So, when you increase the hydrogen partial pressure, to increase the temperature, you see you need to have high chromium content and high moly content.

Again, there is a limit beyond certain hours, you see that if you increase you know beyond and beyond certain partial pressure of hydrogen, if you increase the partial pressure of hydrogen, again what happens? The temperature over which the reactor can be subjected can be reduced. This is the relation between the temperature of the reactor and the partial pressure of hydrogen in the reactor.

If you increase the partial pressure, the temperature at which the reactor can be safely operated is decreasing now. But you want to increase the temperature and you increase the partial pressure of hydrogen, then you go for high chromium and high moly content ok.

So, this is a way, the material is selected for the reactors, where decarburization is a major problem. By the way, the chromoly steels are also known for creep resistance right. In order to have high creep resistance, people go for chromoly steels; in fact, it goes both ways ok.

If you more problems, you go for five chromium. For example, you can go for it you can go for 9 chromium so that the stability of the steel against decarburization increases with more chromium content. The chrome moly steels are better materials for environments, where the decarburization is a problem ok.

So, this is about the decarburization and these curves are called as Nelson curves. Please look at this the decarburization is a high temperature phenomenon and it is a chemical reaction taking place. In the case of hydrogen embrittlement, it is ambient temperature phenomena and it is a more of mechanical loss in ductility because of embrittlement taking place.

It is not an embrittlement here, here because of loss in carbon, the strength of the steel significantly reduced and beyond that it is high temperature process, you can have a molecular hydrogen here, you can have atomic hydrogen here; both can cause problem as far as the decarburization is concerned.

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Hydrogen Attack<br>High temperature process<br>Cu-base alloy (Cu-Be)<br>Cu<sub>2</sub>0 Oxide michusions are present CDEEP<br>IIT Bombay MM 713 L 3 2 Slide 19 Anneal<br>CU20+2H and CU+H2O.<br>H com diffinse into the metal, water steam<br>builds up pressure and course cracking.

Let me go to the last topic of hydrogen damage that is called as hydrogen attack. This again is in high temperature process. It is found to happen especially in copper base alloys; especially, in copper beryllium alloy systems; copper beryllium is used you know the strength of copper beryllium is very high.

In the copper base alloys, assume that you have  $Cu<sub>2</sub>O$  in oxide inclusions are present and if you anneal this, sometime what people do is you know when you have highly rolled work hardened aluminum, I am sorry copper alloy and you want to remove these the residual stresses, you anneal at high temperature in hydrogen containing atmosphere.

So, that the copper is not getting oxidized. It is reducing atmosphere. But if you are going to have it at other temperature, what it can happen is you can combine with this and you can form steam. So, hydrogen can diffuse into the metal and you can form water. Please notice the water is at a higher temperature. At higher temperature, what happens now? This will be in form of a this will be in the form of a steam. So, builds up pressure and cause cracking.

So, it is an internal cracking. It is happening because of hydrogen atomic hydrogen getting into the copper base alloy. Please notice copper is noble compared to hydrogen, that is why hydrogen can reduce copper cuprous oxide leading to copper and water. Because of high temperature, the water becomes a steam because of higher volume, it leads to a cracking process. So, this is a you know we term it as a hydrogen attack in high temperature process ok.

So, any questions in this so far? There are no questions, I think this brings us to end of our discussion on stress corrosion cracking and hydrogen damage of metals.