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Lecture – 16 Corrosion – V

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Hello, in this talk we will discuss about two important forms of Corrosion that is a very much dependent on the stress. And or maybe stress is associated with these two types of corrosion; one is stress corrosion cracking, another one is hydrogen embrittlement. So, both the kinds of corrosion are very important forms of corrosion and you have to understand that those are dependent on the microstructure and very must specific to the environment.

So, if you talk about stress corrosion cracking, you will find that deep particle this particular kind of corrosion is not experienced by all materials in all environments as you see in general corrosion and or maybe like pitting corrosion or crevice corrosion. So, this is very much dependent on the environment specific, it is very dependent on the environment. Similarly, hydrogen embrittlement also is very much dependent on the environment.



So, you will find that this can be a kind of major cause of failure of different component and in very much important engineering sectors, like this is the case for left side the collapse of pre stressed concrete beam of a laboratory roof after 35 years of use is shown. So, you will find that how badly it has been collapsed and this is particularly in breeze, roof this is a major cause of failure which are actually unnoticed sometimes.

Because, you will find that the there is always seepage of the water or maybe the environmental species through the porosities in the concrete and as a result of which it basically corrodes the underneath steel. So, where it is subjected to any load or any stressed naturally it can go it can fail very quickly. And the failure of the stress corrosion cracked component is so fast that you cannot really mitigate it at that time, like in other case of other form of corrosion like general corrosion or pitting corrosion.

So, in stress corrosion cracking the kinetics of failure is much faster. So, you cannot as soon as you start spelling you want to notice it collapses all on a sudden. So, stress corrosion cracking is a very dangerous form of corrosion. So, at the right side there fracture of pre-stressed cable in the moment tension zone is shown. So, how badly it has failed it is understood from the particular picture.

So, you can understand the stress corrosion cracking can be the major cause of damage of roofs and then bridges and weak structures which under goes which is which as subjected to stress and in corrosive media.

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So, for this stress corrosion cracking to occur it is very much important that you have stress in the environment not only the externally applied stress, but it may be the internal stress like residual stress in the component; so, it can also lead to the failure its service. So, stress from this may be from any source either external source or internal source and in the environment there has to be corrosive species. So, when the component is subjected to both the external factors, it leads to that corrosion or failure there it faces failure by the process of stress corrosion cracking.

So, if you quickly go through that microstructure of stress corrosion crack product you will find that in the microstructure. There are if that particular stress corrosion cracking basically usually proceeds by intergranular fashion, sometimes it may also proceed through trans granular fashion, but mode of failure is usually brittle in nature.

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lloy	Environment				
arbon steel	Hot nitrate, hydroxide, and carbonate/bicarbonate solutions				
ligh-strength steels	Aqueous electrolytes, particularly when containing H ₂ S				
ustenitic stainless steels	Hot, concentrated chloride solutions; chloride-contaminated steam				
ligh-nickel alloys	High-purity steam				
-brass	Ammoniacal solutions				
luminum alloys	Aqueous CI", Br", and I" solutions				
itanium alloys	Aqueous CIT, BrT, and IT solutions; organic liquids; NoO4				
fagnesium allovs.	Aqueous CI ⁻ solutions				
irconium allovs	Aqueous CT solutions: organic liquids: L at 350 °C (660 °F)				
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Metal or alloy	Environment	Initiating layer			
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Metal or alloy α-brass, copper-aluminum Gold-copper	Environment Ammonia FeCl3 Acid sulfate	Initiating layer Dealloyed layer (Cu) Dealloyed layer (Au) Dealloyed layer (Au)			
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So, now as I mentioned you that the stress corrosion cracking is very much environment specific all alloy is they do not undergo stress corrosion cracking in all environment. So, these are the environment materials combinations where stress corrosion cracking behavior have observed till date. But again it is a kind of very open field in many alloy in environment. This particular environment where it undergoes stress corrosion cracking is not known, because this particular observation is also very much painstaking.

So, you have to wait for several hours for the data to have and then you have to notice that, and you have to basically document everything. So, this is a kind of open field of research where many of the researchers are also not will willing to work on, because again this is a very much conventional field of research takes lot of time, lost lot of observations skill. So, this is very much open field for future research as well.

And in many alloy environment it is not understood when the stress corrosion cracking you will start and what is the stress corrosion cracking behavior of the component in a in a particular environment. So, these are typical atrocity you that alloy involvement combinations where there it is establish the stress corrosion cracking will occur, like carbon steel usually undergo stress corrosion cracking in hot nitrate, hydroxide and typically the carbonate solution. High strength steel undergoes stress corrosion cracking in aqueous electrolyte, particularly which contains sulphur dioxide which contains the hydrogen sulfate.

And in the case of austenitic stainless steel it undergoes stress corrosion cracking in sodium chloride containing environment high nickel alloys undergo stress corrosion cracking in high purity steam. Alpha brass undergo stress corrosion cracking in ammonia occur solution, aluminum alloys, titanium alloys, magnesium alloys, zirconium alloys are undergoes stress corrosion cracking in chloride containing, moment containing or iodide containing solution.

Similarly, alpha brass again you will find that that for usually, what does it observe that it is very important to know that why this particular stress corrosion cracking behavior is environment specific. Because it has been observed that be no reason behind the stress corrosion cracking is the selective leaching of the typical passive film which forms on the surface.

So, whenever there is leaching of the passive film, which are formed on the surface usually it acts as a kind of zone where there is again macro galvanic attack. And then where stress is very high stress concentration occurs so, it under goes dissolution at a much faster rate. So, the environment is that environment where there is reaching of the typical passive film. So, if you say the case for different alloys as discussed above like alpha brass which undergoes stress corrosion cracking in ammonia occurred solution.

So, if you see the initiation layer it is the d alloyed layer of copper. So, there is de alloying and as a result of which you will find that the naturally in that zone there is stress concentration and subsequent dissolution at a much faster rate. So, stress corrosion cracking behavior is observed in that case. Gold copper system and ferric chloride again this is the alloyed layer in the iron chromium nickel. Saline iron chromium nickel based alloy in chloride hydroxide or (Refer Time: 07:32) water containing environment, again there is de alloying phenomena. So, in alpha brass nitrate solution nitrate solution there is oxide formation.

In ferrite ferritic steel high temperature water solution there is any oxide formation, nitride formation, titanium alloy hydride carbide. So, you can understand that these all carbide, nitrate, hydride they are again quite porous in nature and those oxides which are found by highly porous and also they are not protective. So, as a result of which the corrosiveness of that particular zone increases and resulting in which there is a initiation of the typical corrosion at a much faster rate.

Similarly, if you take the case for titanium alloys in chloride containing environment you will find that at that particular contact zone there is hydrate formation. This hydroid is not really a if very much ductile in nature it is highly brittle in nature. So, when the component is subjected to stress, you will find that there is a brittle in phenomena and as a result of which the crack formation starts from the hydride formed region.

So, that environment metal combinations are very important, because first of all so, you can understand that the reason behind the stress corrosion cracking is our maybe well it a few more few there are different regions who which are responsible for stress corrosion cracking.

First region is the selective leaching or maybe selective leaching of the damage of the typical passive film which protects the surface. Second region is that there may be some hydride or other alloy for other compound formation, which are not really protective neither protective not quite ductile which are highly brittle in nature. Third region maybe some other phase formation which are porous as compared to that term in contrast to that of passive fame, which were needed to form for protection against the corrosion in that environment.

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So, these are different regions for the stress corrosion cracking, now and as a result of which unless and until, these particular conditions are satisfied the component do not undergo stress corrosion cracking. And as a result of which you will find that the alloys

are very much proved to stress corrosion cracking under specific environmental condition.

So, if you quickly go through the stress corrosion kinetics of the stress corrosion cracking or if you see the stress which are essential for stress corrosion cracking to occur. You will find that there is a threshold stress which is essential for the initiation of the stress corrosion cracking, and then you will find that it propagates such a much much faster rate.

So, if you see the time for initiation at time for the propagation of the stress corrosion crack sample, you will find that when the threshold stress is when the stress is much lower than that of threshold stress there is no stress corrosion cracking at all. So, these stresses nothing but actually the stress required for the breakage of that particular crack, for particular exposed component which are where there is formation of the passive film.

So, you have to be very much careful in choosing the stress in that corrosive environment. So, if you choose the stress properly, you will find that the component does not undergo any kind of stress corrosion cracking. So, frankly speaking if you can avoid the stress corrosion problem, if you just use the component at a stress much lower than that of threshold stress required for the stress corrosion cracking to occur.

So, stress corrosion cracking diagram is very important or mapping is very important, for a specific alloy system, for a specific environment for choosing the alloy for that particular power in that particular environment. But, you have to understand that this threshold stress is can be much lower than that of UTS or sometimes yield strength of the material.

So, usually the component fails under stress in corrosive environment, when it undergoes stress corrosion cracking at a stress much lower than that of yield strength of the material. So, you cannot really predict the stress corrosion cracking behavior or you cannot design the component based on the its behavior in the simple environment where there is no corrosive fluid.

On the other hand, as you increase the stress, above threshold stress you will find that there is a time of crack initiation at track time of crack failure. Actually, it increase it basically there are particular stress, there is crack initiation and a particular stress much higher than that of crack initiation there is crack propagation. So, this particular difference between or the range between crack initiation, the time required time range between crack initiation and crack propagation, actually decreases as you go on increasing the applied stress on the surface.

So, this is very important when the stress is quite low time required for initiation at, time required for failure is quite high as you go on increasing the stress. The time where for time for crack initiation at time for crack growth actually crack propagation decreases. And as you go on increasing the stress further then again it decreases to a large extent and finally, it fails.

So, this is very important and whenever you do stress corrosion cracking study, you have to note down these two time one is crack initiation time and crack propagation time. And if you just draw the crack initiation time as a function of applied load and crack propagation time as a function of applied load, that is nothing but your stress corrosion cracking mapping or behavior of the alloy in the stress corrosion cracking environment.

Now, if you quickly go through this particular magnitude of the crack tip stress distribution, as a function of the like critical fracture stress intensity factor. You will find that it basically consists of three important they are like stress initiation threshold stress intensity for stress corrosion cracking, this is the initiation and then it propagates and finally, leads to failure.

So, total time for that typical stress corrosion cracking may be divided into 3 tie 3 different time regime. One is the stress corrosion cracking the time required for initiation, then plateau region where the stress corrosion cracking rate is almost same and then finally, trans that another region where then the rate of stress corrosion cracking is much faster.

So, in this region usually there is a that feel film dissolution rate is much lower as shown as film dissolution at this threshold stress there is dissolution which starts then as you go on increasing the stress and you and all corrosiveness in the environment. You will find that the stress corrosion cracking resolution rate is much lower at the steady region there is dissolution and formation rate. And after that you will find that dissolution rate actually exceeds that of rate of pre formation. So, as a result of which there is rapid failure of the component. So, it is very important to do that film dissolution rate or film rupture rate and also formation rate at a specific under specific stress condition.

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So, usually you cannot show, you can say that say the stress corrosion cracking process and under two stages; one is initiation of the stress corrosion cracking another one is propagation of the stress corrosion cracking. Through initial stage initiation is very important because you can control the initiation of the stress corrosion cracking by different precautionary measured. But as soon as it initiates it is very difficult to control the propagation, because propagation occurs at a much faster rate leading to the failure of the component.

So, if you talk about the initiation usually for initiation as I mentioned you there are different reasons for the initiation of the stress corrosion cracking; one of the important region is the presence of imperfections or porosity is on the surface. So, whenever you keep the component in that environment where there is a pit formation or there where there in that particular use the component with the surface condition, where there are lot of imperfections of the surface those sites actually act as a site for the pit initiation or may be crack initiation.

So, you will find that you if you just go on having the surface, you will find that initially when there are very small defects on the surface there is no initiation. So, after a certain period of time then there is no again initiation starts. And after a certain period of time further you will find that there is slow growth of the cracks through the imperfection sites because there is stress concentration and also dissolution of the film further.

So, by the typical galvanic action and then after it reaches a certain length you will find that there is propagation and which is very difficult to control. So, it is dependent on the fracture toughness of the component and also the scale which is forming.

So, you have to ensure interested to get rid of stress corrosion cracking problem, you have to control the initiation stage very nicely, you have to see the surface properly. So, that surface is free from any kind of flaws, there are no defects on the surface and also there is no loose (Refer Time: 17:16) from the surface they so, that there is pitting attack or micro galvanic attack or any other attack. So, you have to control the initiation stage very nicely by checking the surface properly.

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So, as I mention you that the stress corrosion cracking in these are the stress corrosion cracking cross section of stainless steel; one is it chloride environment another one is in light water reactor light water reactor normal water environment says, it is stainless steel which undergoes cracking by typical inter granular cracking for mechanisms. So, here you will find that stress corrosion cracking actually starts from the surface, but it

also there are also crack formation and inter granular fashion all throughout the material up to certain day.

This is the transgranular fashion where chloride environment is responsible, where a transgranular fashion it can also proceed because of presence of lot of porosities or reaching of the film in different regions not necessarily along the grain boundary regions. So, the usually though it process through intergranular fashion, but it can also process through this transgranular fashion so, but overall mechanism is basically overall mode of failure is by brittle by is brittle failure.

So, if you quickly have the map of the material environment and that of stress you will find that the stress corrosion cracking, usually is observed in that particular overlap region where there is material undergoes corrosion in corrosion of environment. It can also undergo fatigue or maybe corrosion fatigue in that under stress; when the stress is fluctuating in nature and in between there is the stress corrosion cracking of the component. So, you have to know these region properly so, that you can get rid of this particular problem by choosing proper environment and stress.

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Now, if you quickly go through the mechanism as I mentioned you that there are different mechanisms which are actually, but most important mechanism is that there are different mechanisms which have been proposed to explain the stress corrosion cracking behavior of different materials. But dissolution and then stress assisted stress assisted dissolution and rapture of the film is the main reason for that particular stress corrosion cracking to proceed.

But if you quickly go through the different micro mechanism, we will find that or different factors responsible for the stress corrosion cracking. There may be metallurgical factor, they may be dissolution factor, they may be mechanical factor, they may be hydrogen factor hydrogen may also assist the stress corrosion cracking.

So, if you quickly go through the metallurgical factors responsible for the stress corrosion cracking, their dislocation co planarity then stress aging, micro segregation, adsorption these all phenomena are observed in stress corrosion crack system. So usually, you will find that when dislocations have (Refer Time: 20:23) in a kind of coplanar fashion; then naturally, the crack propagation is basically it is very easy as compared to that of dislocation entanglement.

And stress aging phenomena when is there again micro segregation phenomena they are they naturally along those sides you will find that there is differential formation; differential phase formation and differential chemical attack electrochemical attack. As a result of which you will find that those regions are corroded as a much faster rate as compared to that of surrounding region. So, the corroded region acts as a zone for the crack initiation. Similarly, when there is adsorbed layer because of the adsorption it reduces the bond strength, again by this decreasing bought strength you will find that region gets weak and crack formation gets easier.

So, metallurgical factors are very important which are responsible for stress corrosion cracking, then hydrogen also can assist a stress corrosion cracking. Particularly, in those cases which are very much hydrate former like titanium. So, hydrate formation if is there the naturally there is embrittlement of the surface; so, along the embrittle surface you will find that there will be crack initiation and propagation at a much faster rate.

Dissolution also is a main phenomena you will find that, when there is a weakening of the bond you will there is faster rate of dissolution; dissolution rate is much faster. There is field formation cracking wall, then again that is there actually you will find that when there is a dissolution phenomena and also film formation. In a discontinuous fashion, you will find that galvanic attack becomes more prominent over there. Then noble element enrichment, then film rupture, chloride ion migration these are again different other factors which lead to dissolution at a much faster rate. And particularly, there is preference cell dissolution. When there is preferential dissolution then only there will be stress concentration and as a result of which there will be preferential crack formation and crack growth in that region.

And mechanical factor which are responsible unlike tunnel pitting and tearing, corrosion product wedging. Those particular factors are responsible because they lead to differential again mechanical forces acting on different regions. As a result of which there is cracking along the certain directions of the material as compared to that of other rest part of the material.

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So, you can say that here in stress corrosion cracking stress is preferentially acting on a certain point and which is so high that, there is cracking of the component at a much faster rate by thinning down of the overall surface area. So, this is the typical case where the (Refer Time: 23:09) stress corrosion cracking are shown. So, this is the particular metal where there is applied stress and which is in also exposed to the self corrosive environment.

You will find that initially mass transport is there along the crack or away from the crack tip and then that mass which are transported from the solution towards the metal surface.

They react in the solution near the crack and then there is adsorption of those species on the surface, because of adsorption of the species.

They can also diffusing and they also can react with the quite particular wall of the material and they can be absorbed in the bulk. And there is bulk diffusion at plastic zone ahead of the adversity chemical reaction in the bulk and then there is bond rupture and then crack propagation. This is that (Refer Time: 24:08) way by which the crack propagates in stress corrosion cracking.

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Now, if you see the interface and also the surface as well as the cross section of the stress corrosion crack product, you will find again you will find this case it has propagated along the grain boundaries. So, it is basically it has propagated in an intergranular fashion, if you see the surface has becomes so brittle, a lot of corrosion product is also there in the form of weights. So, these all things you will observe in the stress corrosion crack surface.

So, if you quickly go through the stress corrosion cracking problem and if you think of its mitigation, the best way to mitigate or to minimize the probability of stress corrosion cracking is by choosing proper material in proper environment. And second way to get rid of this particular problem is by reducing the stress level of the material particularly inter particularly the internal stress which is present in the component. And of course, by the application of inhibitors you can reduce the aggressiveness of the environment by the application of the cathodic protection, you can also reduce the stress corrosion cracking tendency to a large extent.

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Second type of problem is hydrogen embrittlement; hydrogen embrittlement is a phenomena which occurs in that environment where there is presence of hydrogen. You will find that hydrogen is very dangerous species, because it can cause the failure by its typically reacting with the surface as by formation of hydrides. So, those hydrides are not really good because those hydrides are very much brittle in nature, in some of the metal it happens.

Some of the metals hydrogen species can diffuse in and in the form of atoms and they just changes from atomic hydrogen to molecular hydrogen in the metal deep inside the metal. And by that conversational process conversation process, they apply lot of pressure and by that pressure, you will find that there is typical blistering inside the surface. That can also called a lot of soling effect inside the component, that is also called the that also calls the embrittlement of the component.

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	Hydrogen embrittlement			Hydrogen attack	Blistering	Shatter	Micro-	Degradation	Metal
	Hydrogen environment embrittlement	Hydrogen stress cracking	Loss in tensile ductility			cracks, flakes, fisheyes	perforation	in flow properties	hydride formation
Typical materials	Steels, nickel- base alloys, metastable stainless steel, titanium alloys	Carbon and low-alloy steels	Steels, nickel- base alloys, Be-Cu bronze, aluminum alloys	Carbon and low- alloy steels	Steels, copper, aluminum	Steels (forgings and castings)	Steels (compressors)	Iron, steels, nickel-base alloys	V, Nb, Ta, Ti, Zr, U
Usual source of hydrogen (not exclusive)	Gaseous H ₂	Thermal processing, electrolysis, corrosion	Gaseous hydrogen, internal hydrogen from electrochemical charging	Gaseous	Hydrogen sulfide corrosion, electrolytic charging, gaseous	Water vapor reacting with molten steel	Gaseous hydrogen	Gaseous or internal hydrogen	Internal hydrogen from melt; corrosion, electrolytic charging, welding
Typical condition:	10 ⁻¹³ to 10 ² MPa (10 ⁻³⁰ to 10 ⁴ pri) gas pressure	0.1 to 10 ppm total hydrogen content	0.1 to 10 ppm total hydrogen content range of gas pressure exposure	Up to 10 ³ MPa (15 ku) at 200– 595 °C (400– 1100 °F)	Hydrogen activity equivalent to 0.2 to 1 × 10 ⁵ MPa (3–15 ksi) at 0–150 °C (30– 300 °F)	Precipitation of dissolved ingot cooling	2 to 8 × 10 ⁶ MPa (30-125 kti) at 20- 100 °C (70- 210 °F)	1-10 ppm hydrogen content (izon at 20 "C, or 70 "F) up to 10 ⁵ MPa (15 ksi) gaseous hydrogen (various metals, T > 0.5 melting point)	0.1 to 10 ² MPa (15– 15,000 pri) gas pressure hydrogen activity must exceed solubility limit near 20 °C (70 °F)
	Observed at - 100 to 700 °C (-150 to 1290 °F); most severe near 20 °C (70 °F)	Observed at - 100 to 100 °C (-150 to 210 °F); most severe near 20 °C (70 °F)	Observed at - 100 to 700 °C (-150 to 1290 °F)		***				***
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So, if you see the different reasons behind this hydrogen embrittlement and their effect it may be of several like and depending on the material it changes. Particularly, if you see the material and environment as well as the type of hydrogen attack absorbed by different materials they are of white types actually. So, like steel nickel based alloy metastable stainless steel here, there may be the hydrogen stress cracking carbon alloy.

This here you actually hydrogen environment embrittlement is observed and that of typical condition is 10 to the power minus 12 to 10 to the power 2 MPa pressure gas pressure, when the gas pressure is increased then there is also problem of the stress corrosion cracking which is called hydrogen stress cracking.

And usually, carbon and low alloy steels are subjected to this kind of problem there is loss of tensile strength, tensile ductility of the component. When again, stress is similar to that of this particular hydrogen stress cracking, but there is loss of tensile ductility which is observed in steels nickel based alloy, beryllium copper bronze, aluminum alloys.

Typical hydrogen attack is observed in carbon and low alloy steel in gaseous hydrogen environment where pressure is even higher. Blistering is a phenomena which is observed in steel copper aluminum based alloy where the diffusion of hydrogen atom through the component is responsible. So, there is diffusion of hydrogen atom and they converts from diffused atoms to molecules and then apply pressure by that process there is lot of swelling in the component when it particularly exceeds the little strength of the material. And you will find that there is local blister formation inside the component.

There is shattering or effect also shattering or shattered cracks or fisheyes formation is another kind of hydrogen assisted embrittlement or cracking or damaged phenomena. Where; what happens is that this is a when the stress is a little bit higher than that of this particular 0.2 to I mean higher than that required for blistering.

You will find that the surrounding area get fractured and the component looks like typical flakes or fisheyes there is micro perforation phenomena. Again at a very high hydrogen contain and similarly and finally, there is hydride formation and depletion of the flow property. So, several things can we have can happen when hydrogen is there in the environment. So, whenever hydrogen is there in the environment, you have to be careful in using the component.

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So, you will find ductility loss of several austenitic stainless steel in high pressure hydrogen. So, ductility actually reduces from 50 percent to as low as 0.1 percent. So, there you have to be careful when there is hydrogen in the environment because it can cause loss of ductility to a large extent. So, if you are interested to get rid of this hydrogen assisted embrittlement, hydrogen can also assess the stress corrosion cracking phenomena.

So, if you are interested to get rid of this particular problem, you have to use proper materials and you have to get rid of hydrogen in the environment. There are several inhibitors available which take away the hydrogen from the environment, inhibitors also play a very important role in changing the environment. So, you have to use the proper inhibitor and also you have to toughen the component or change the composition. So, that it does not undergo any cracking in a presence of hydrogen and also you have to be very much careful in using the proper processing technique.

So, that there is no chance of hydrogen generation in that particular processing; particularly, when you undergo any welding operation you will find that from the welding electrode there is chance of a lot of hydrogen pickup. So, if you choose proper welding electrode proper coated electrode. So, that there is no hydrogen in the environment you can get rid of this problem to a large extent.

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So, thank you very much.