Corrosion Failures and Analysis
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Lecture - 23
Intergranular Corrosion: Knife Line Attack and Prevention Methods

Let us start lecture 23. So, this is the course on Corrosion Failures and Analysis, and we discuss Intergranular Corrosion. And today, we will conclude this intergranular corrosion, and next day onwards we will start discussing Crevice Corrosion, ok.

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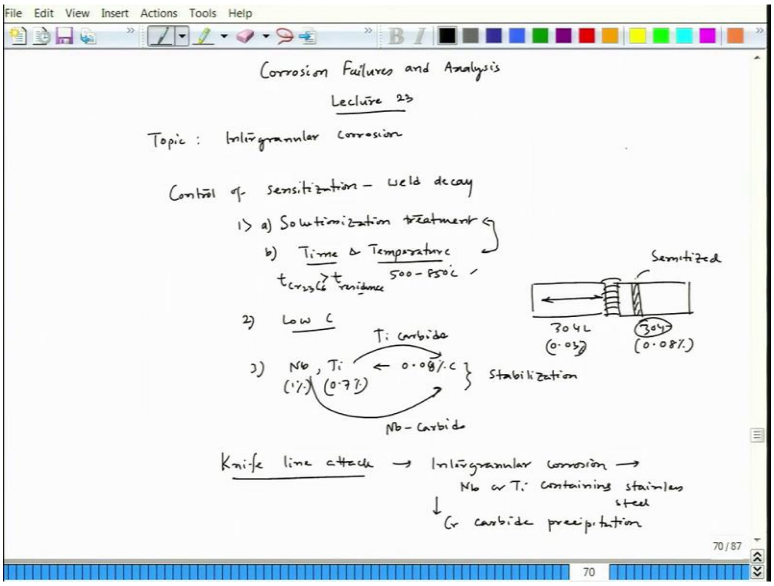

So, the course is; and if we recall our discussion in last two lectures, we talked about the mechanism of intergranular corrosion which relates to the chromium depleted zone formation, due to chromium carbide precipitation along the grain boundary in case of 304 stainless steel.

And that chromium depleted zone acts as a narrow anode and all other areas are large cathodes. So, that is what it becomes a serious galvanic corrosion along the thin strips, where chromium depletion happens along the grain boundary and that initiates intergranular corrosion.

Now, at the same time we talked about weld decay. In case of weld decay, what happens you start with homogenized 304 stainless steel, where chromium is all over the matrix as well as grain boundary are uniform is uniformly placed, ok. So, where everywhere it is 18 percent which is sufficient for a very good passivation to achieve.

Now, during welding of two components what happens, in the weld zone the temperature is maximum, but away from the weld zone, at a zone we have shown by putting thermocouples that in that zone the temperature reaches, temperature is between 850 to around in that temperature zone 500 to 850 degree Celsius. The material stays for a longer period, and that initiates chromium carbide precipitation in that zone only.

Rest of the zones we do not have any problem, either chromium carbide dissolves and it homogenizes or if the temperature is higher than 850 degree Celsius which is between those zone and the weld pool. As well as if you have move away from that zone you will get the temperature does not reach to that 500 degree Celsius. So, there is no problem of having chromium carbide precipitation. In the zones, away from those that particular temperature section where material stays for longer period at 500 to 850 degree Celsius. So, that is called weld decay.

And now question is how to stop that weld decay. There are 3 processes one is. So, we talked about control about control of sensitization or you can say weld decay. So, there are 3 processes, in 1st process we have solutionization treatment by chance if the material has sensitization, has got into sensitization mode, one can heat it to around 1050 degree Celsius where chromium carbide dissolves and makes it homogeneous distribution of chromium. So, the problem is resolved.

And then after heating there for some time once chromium dissolves then you quench it quickly, so that chromium carbide does not precipitate anymore when the temperature, when during cooling, when the material goes through that 500 to 850 degree Celsius. Since its quenching though not much of time is available for chromium carbide formation. So, the problem is resolved.

And then solutionization treatment and another part is you do not this is let us say 1, and let us say you time and temperature both are important. So, this is 500 to 850 degree Celsius and this time you can say that time for $Cr_{23}C_6$ is should be greater than time of residence particular temperature zone. So, then chromium carbide does not precipitate.

So, now, this two are interrelated. So, interrelated in the sense that during solutionization you have to heat it higher than this temperature zone and then dissolve chromium carbide or other way around that you do not go to the during welding itself first stage, your cooling should be fast enough. So, that when it passes through that temperature zone time is not available time is short enough, so that chromium carbide does not precipitate. So, this is the part one.

Second is one can use low carbon. We have also seen with the help of time temperature sensitization diagram that if the carbon content goes below 0.03 percent, the time required for precipitation of chromium carbide would be very high around close to 6 to 7 hours, in case of 304 stainless steel; if you reduce the carbon below 0.03 percent. So, that case there is no question of sensitization because whatever cooling you employ you do not usually keep it that long in that particular temperature range. So, no question of sensitization. So, that can stop it.

Now, in that regard let us say if you have two sections, one is 304 let us say 0.03 percent carbon, so where this is considered as L. And then, another one block let us say another thick plate you take 304 which is normal 0.08 percent carbon. Now, if you weld them, you would see that sensitization would be experienced in case of 304, 0.8 percent, and this part this entire part would remain unsensitized, and this is sensitized, fine. So, this situation you can come across.

And the 3rd process what we done what we have thought, that we put niobium or titanium into the metal in a small amount. So, niobium about 1 percent, titanium around 0.7 percent. So, that they take care of carbon, and then does not they do not allow sufficient carbon availability for chromium to get chromium carbide precipitation to have chromium carbide precipitation.

Now, this is added in case of 0.08 percent carbon steel carbon stainless steel, that means here you do not go for a low carbon you have a normal carbon content what is there in 304, you add titanium and niobium. So, problem will be resolved, because they will take care of this carbon and they will form niobium carbide or titanium carbide and they do not allow chromium carbide to form because there is not much of carbon available.

So, if chromium carbide does not form the chromium distribution would be homogeneous and it will be in solution it will lead to strong passivation of the stainless steel. And that is what we need for stainless steel to have stainless property, ok. So, these are the 3 major routes where through which we can avoid sensitization.

Now, question is we talked about one particular situation that knife line attack, ok. So, in case of 304, 0.8 percent the sensitization happens because of weld decay, but knife line attack is also related to intergranular corrosion, but it is in niobium or titanium containing stainless steel. And this particular process we call it stabilization.

Why it is stabilization? We are actually stabilizing carbon, and making we are actually taking carbon and then making the stainless steel stabilized against sensitization. Now, this is this intergranular corrosion in knife line attack, they are interrelated and this also related to chromium carbide precipitation chromium carbide precipitation.

Now, interesting part is when we talk about this chromium carbide precipitation that means, it must be related to that situation that niobium and titanium carbide they do not form rather chromium carbide form specifically. So, that means, stabilization action is totally lost. So, we have to understand that mechanism of knife line attack, mechanism.

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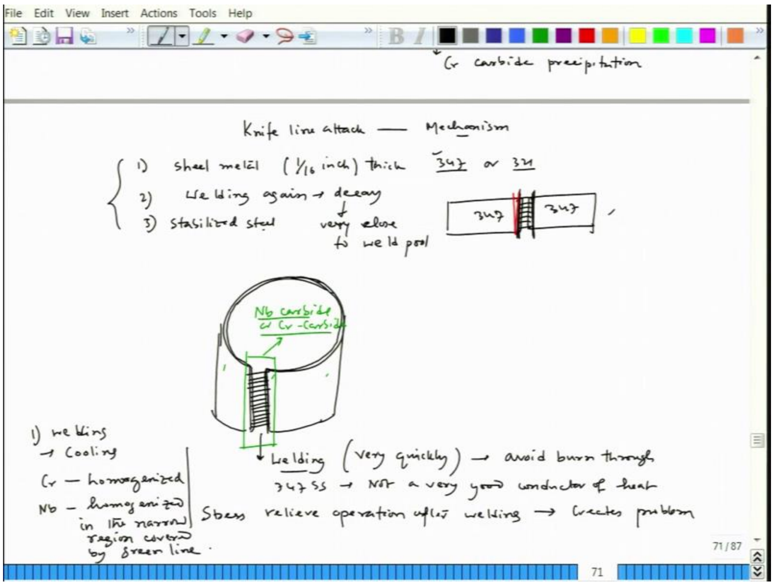

Now, 1st thing this happens in case of thin sheet metal, ok, around 1.16 inch thick. Those kind of sheet metal when you and sheet metal of definitely let us say 347 which is a stabilized stainless steel or 321, ok. So, 321 contains titanium, 347 niobium. Now, 2nd part is this is related to welding again. 3rd part is it happens, so if you consider weld decay as well as let us say you have a thick plate of 347 and that is two 347, and these are thick plate thicker than let us say 2 inch, above 1 inches thick or something like that.

So, that time if you weld you do not experience any weld decay, ok. But if it is thin enough then what happens? If it is thin, so then that particular knife line attack happens very close to that weld part, ok, very close to that weld part. In fact, the main difference between weld decay that is observed in case of 304 and the knife line attack that had that happens in stabilized steel, the weld decay happens quite a substantial distance from the weld pool and the knife line attacks happen a very close to the, very adjacent to the weld pool that is the main difference.

And interestingly one more thing let me just since this particular picture is also there. So, if you take instead of 304, if you take 347 in one side, the another side is 304 0.08 percent and this is also 0.08 percent carbon, fine. So, both have same carbon level, but still the situation would be same the 304, 0.8 percent carbon would get sensitized in that weld decay portion, but in 347 we will not experience any weld decay, ok.

So, that this is again a welding again, but the difference is it is also a kind of weld decay you can say, but this decay happens very very very close to weld pool, ok. And this is much closer than what we experienced in case of weld decay in normal thicker plate of 304, fine. So, this is and this happens in stabilized steel.

For example, in this example, we have one side stabilized and one side 304 steel, but since it is a thicker plate knife line attack does not happen in 347, but weld decay happens in 304. So, this is the main point in case of knife line attack. And why knife line attack? Because this particular failure happens in a very sharp manner, ok. So, it is a very sharp manner. So, it looks like a sharp needle like knife which is going through the sheet metal, ok. So, that is what this name comes knife line.

Now, in order to understand the mechanism we have to see keep see about this welding part, we have to carefully observe this welding part. Since, it is a thick thin metal sheet, so let us say this is the let us say this is a kind of drum one is making out of this thin sheet metal, ok. This is a very thin sheet metal, ok.

So, this is the drum one is making. So, now, after that you have to join here, let us say this is welding. Since, it is a thin sheet, ok, so the welding has to be performed very quickly. Why? Just to avoid burn through, ok. So, now this is done very quickly. Second thing is let us say if it is 347 stainless steel, it is not a very good conductor of heat, very good conductor of heat.

So, that means, once you do the welding of the thin sheet the heat is actually centered or constricted in that center pool, in the weld pool section. It does not spread through, ok. And it quickly cools also because it is a thin sheet, so you have lot of surfaces available. So, heat dissipation to the air is very easy.

Now, that is what this particular zone which is very narrow zone of that particular section, narrow zone of the particular section which cools very fair quickly. At the same time the heat is actually centered around that zone. It does not go away to the other part, the what it have, what happens in case of a thicker plate. So, since it is constricted there, now, definitely during welding the temperature goes beyond the melting point of that metal, let us say around close to 1500 or 1600 degree Celsius, fine.

And then during welding, so the during welding temperature definitely goes much beyond that, around close to 2500 degree Celsius. So, it melts, but around that region also the temperature can go up to the level of around close to 1300 to 1500 degree Celsius. Now, due to that temperature, in the beginning, this steel was entirely stabilized only niobium carbide precipitate, no chromium carbide chromium was homogenized.

Now, since that heating has happened in that narrow zone and the temperature reaches beyond 1300 degree Celsius. In that narrow zone, chromium carbide is not there at all, but niobium carbide what was there; what was giving stabilization action of that steel that also dissolves. So, that means, in that narrow zone you do not have niobium carbide, do not have niobium carbide or let me just put it, niobium carbide or chromium carbide, fine, both are not there.

Now, when you quench it or when you cool it fast, ok because cooling of course, happens very fast because of the thinner section. Now, in this zone you do not find any niobium carbide or chromium carbide, but rest of the zone you have chromium and niobium carbide present and chromium is all homogenized.

Now, once it happens then if you do not do anything to that it will not create any problem because there is no question of having chromium carbide formation in that narrow zone even because you have cool it very fast, you have cooled it very fast. So, there is no question of formation of chromium carbide effect.

Niobium carbide does not form again because it cools fast. But rest of the part chromium is homogenized. Here also, now the chromium is homogenized. So, no problem it absolutely, fine. It will work absolutely, fine because there is no question of sensitization. Chromium carbide is not there, no question of sensitization.

Now, the problem happens somewhere else during stress relieve operation because it is a thin sheet and there could be lot of stress inbuilt because of that quick cooling after heating to a very high temperature of the thin sections, there could be a possibility of warpage because thin sheet welding always leads to a little bit of warpage.

So, that is what its better and there is lot of strain here, there is not much of strain here, not much of strain here, but here there will be lot of thermal strain. So, that is what one has to do a little bit of stress relief. So, the stress relieve operation after welding that creates problem.

So, now, before stress relieve operation, what are the stages? Welding and then rapid cooling because of the thin sections. So, all over the places you have chromium homogenized and niobium homogenized in the narrow portion, narrow region covered by green line, fine.

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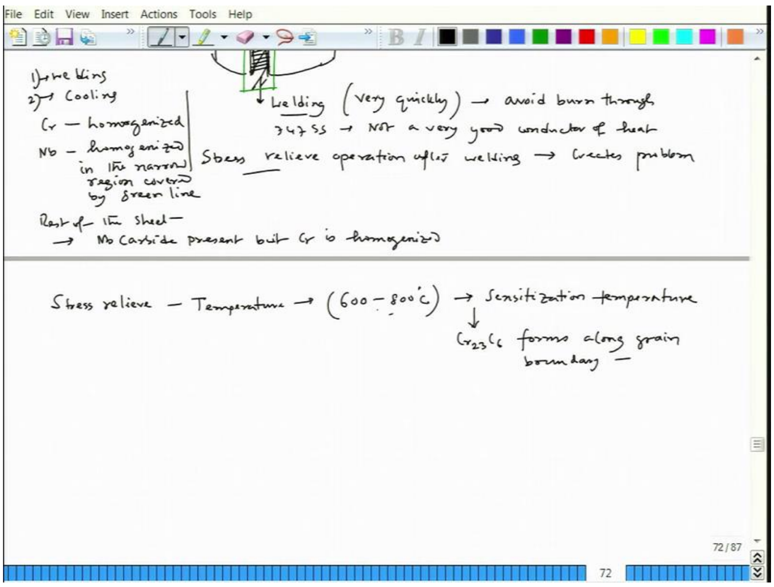

And rest of the part, so this is 2nd part, welding and then 2nd part now, the rest of the part rest of the sheet niobium carbide present, but chromium is homogenized because it is a stabilized steel. Now, during stress relieve what happens the temperature is taken to, temperature for stress relief temperature is around close to around 700 to 800 degree Celsius or sometime you can also have it 600.

Now, you have to keep it there for some time, in this temperature and this temperature you could see that this is that sensitization temperature, sensitization temperature. So, then chromium carbide forms along grain boundary where it forms in this particular zone because rest of the zone you have niobium carbide, no problem. You do not have carbon for chromium carbide formation, even if you heat it there. But in this zone chromium and niobium both are in solution.

So, once you heat it there, the chromium carbide has the formation ability in that temperature zone is much higher, the kinetics of chromium carbide formation is much higher in that temperature zone. Niobium carbide does not form there, so it forms here. So, in order to understand this it is better to draw a semantic plot for the temperature where chromium carbide forms dissolves, as well as niobium carbide forms and dissolves.

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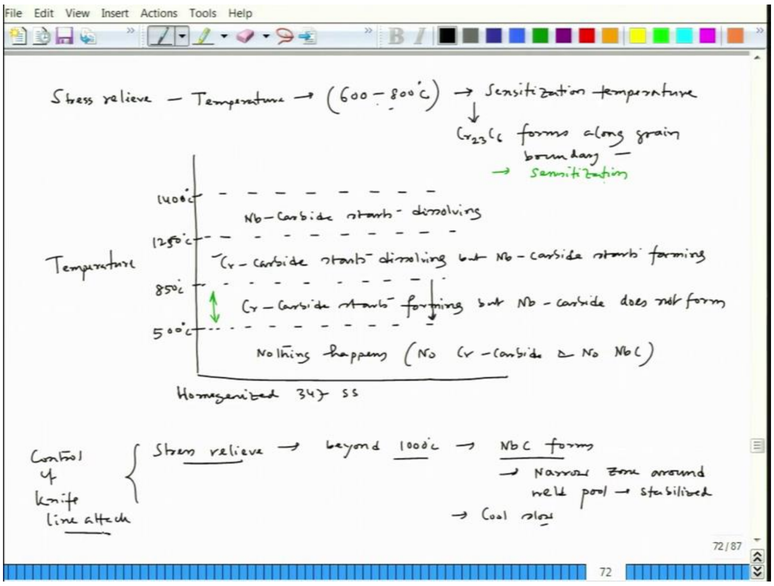

So, in order to do that, so let us see a kind of a semantic plot. Let us say this is temperature, fine. So, let us say this is 500 degree Celsius, let us say this is let us say 850 degree Celsius, then you have around close to let us say 1200 or 1250 degree Celsius and then of course, you can go up to around 1400 degree Celsius like that.

Now, if you see the possibility of chromium different carbides formation as well as their dissolution, below that temperature nothing happens. So, no chromium carbide and no niobium carbide, I am talking about overall behavior. Because if you start with the homogenized steel where niobium and chromium both are there.

So, if you heat it to 500 degree Celsius nothing happens. And beyond 500 degree Celsius chromium carbide starts forming or precipitating along the grain boundary, but niobium carbide does not form. Now, if you go beyond 850 degree Celsius, the chromium carbide starts dissolving, and around 1000 degree Celsius it dissolves very quickly.

So, dissolving, but niobium carbide now starts forming. So, this is to starting material is homogenized 347 stainless steel. Now, beyond 1250 degree Celsius chromium carbide already has dissolved. Now, niobium carbide starts dissolving, ok. So, this is the situation. Now, what happens?

Due to that stress relieve operation which is done within this temperature range, within this temperature range and since niobium in that green colored covered area which is close to that weld zone is also in the solution during cooling stage. So, the first chromium carbide comes out no niobium carbide comes, no niobium carbide forms. And then after that what you do? You quench it, ok. And then, not quench it even you cool it slow because you are doing stressfully even you quench it, again you quench it there will be little bit of strain.

So, you cool it slow. Now, when you cool it slow, then there is no question of niobium carbide in that narrow zone close to that weld pool and there chromium carbide has formed, along the grain boundary. So, then this particular region, this particular section will go to sensitization. But rest of the part we have niobium carbide because it is already stabilized. So, that is what the sensitization problem will be experienced with a narrow zone across that weld pool.

And if we keep fuming nitric acid nowhere things will happen because no corrosion will be observed in other places, other than narrow zone of that weld pool. But there since it is a highly concentrated sensitized zone, we have serious chromium serious intergranular corrosion happening there and that leads to a very sharp failure in the form of knife line, ok.

So, that is what this is called knife line attack. So, that is the basic reason why knife line attack happens. And that happens in case of stabilized steel. So, if you take 321 which is titanium stabilized stainless steel, still it will experience the same knife line attack. So, now, coming to this point that in order to avoid knife line attack. So, how what should be done?

Let us say even if you go for stress relieve operation, the stress relieve see if that is essential, the stress relieving should be done beyond around 1000 degree Celsius, ok. So, what is the advantage? At that time if you see this diagram beyond 1000 degree Celsius chromium carbide dissolves, niobium carbide forms. So, in the narrow zone around that weld pool, niobium carbide forms.

So, once niobium carbide forms, the narrow zone is weld pool is stabilized. Once it is stabilized there is no carbon available for chromium carbide formation, after that you can cool very very slow, ok. You just leave it outside. It will cool down. Nothing happens because there is no question of chromium carbide formation, there is no carbon in there because it is the entire tank is stabilized now, even with that narrow zone also it is stabilized.

So, that should be the practice and then cool it very slow. So, even if you cool slow does not happen, does not does not make any sense, does not make any problem because when it goes through this zone, carbon is not available for chromium carbide. So, sensitization is completely avoided. So, that should be the; that should be the control, fine. So, let me stop here. This is about sensitization and related to intergranular corrosion. And we have also seen that intergranular corrosion happens in case of aluminium alloys also.

We have given one example of aluminium 8090 alloy. Now, before I end I just would like to indicate that sometimes it will be very difficult to find that chromium carbide along the grain boundary even with the help of a very high resolution SEM, it will be very difficult. But recently we have found out, a smart way of understanding whether the chromium carbide forms along the grain boundary and that leads to stabilization, that leads to sensitization.

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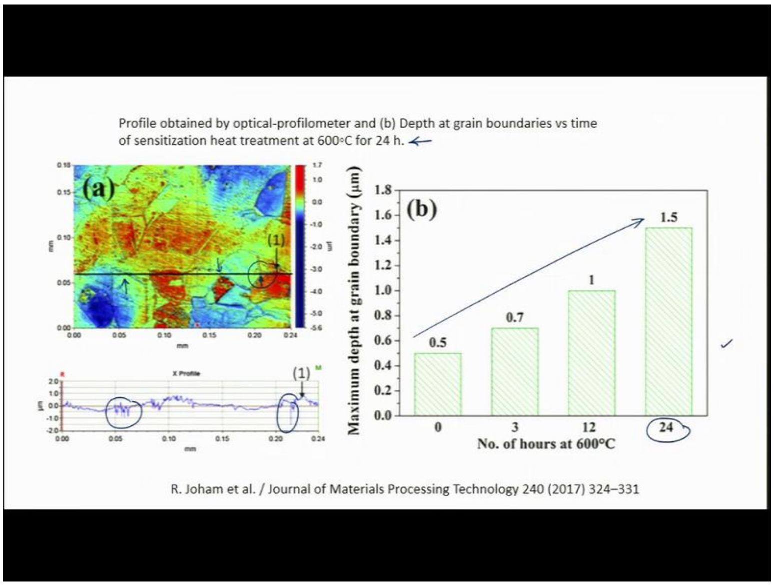

So, this is the work we have recently done at IIT Kanpur. So, what happens? This is a 304 stainless steel and we have heat it to this temperature and 24 hours, because of that that material got sensitized. And this is the sensitization curve, means the depth of attack along the grain boundary. And this is the micrograph.

What we did? We took optical profilometry, the optical profilometry also gives you the undulation on the surface and interestingly if you notice that wherever it passes through the grain boundary, so these are the portion where it passes through the grain boundary this is the portion, you will see that this is the zone where grain boundary, that line is passing through the line of measurement of that optical profilometry is passing through the grain boundary.

And then that leads to you see in the grain boundary region it is a there is a sharp dip. The sharp dip means that particular portion has got attacked very aggressively, even if you consider this particular portion. So, this is particular portion where is this is lying here, ok. So, that portion is actually gone very deep.

And if you see that up to 24 hours the material was heated to 600 degree Celsius and it is simple 304. And you see that the as you heat it, and as you measure this particular depth profile along the grain boundary the grain boundary the depth is gradually, the local attack is gradually increasing and this indicates that the material is sensitized and this happens because of the chromium carbide precipitation. So, this is one a indirect way of proving that the material is getting sensitized and that is actually due to chromium carbide precipitation along the grain boundary.

So, let me stop here with this particular explanation. And now you see this paper you can go through, this is the reference of that particular paper where this data is there. So, you can learn more from this particular paper. So, let me stop now. We will continue our discussion. In the next lecture onward, we will talk about Crevice Corrosion.

Thank you.