

Corrosion Failures and Analysis
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Lecture - 31
Various conditions favoring pitting corrosion (Part 3)

So, let us start lecture 31, and the course is Corrosion Failures and Analysis. And we have been discussing pitting corrosion and mainly the conditions for pitting corrosion. We have discussed 4 conditions till now. One is pitting passivating metal, then chloride ion concentration, and effect of chloride ion concentration, then we talked about stagnant situation. And we talked about presence of oxidizers, Fe plus 3 or Cu plus 2 ions that can lead to pitting.

Because pitting in case of Fe plus 3, it actually raises increases pitting because it actually reacts your gives a negative impression to the passivation. So, that is what pitting starts.

Now in case of copper plus plus it actually gets deposited on the surface and that forms a small pit which actually becomes a strong cathode. So, locally cathodic reaction happens and around that area would have a pit formation. So, those are the situations where we can have pits. Now we will discuss few more conditions and then we will talk about mechanism of pitting.

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Corrosion failures and Analysis

Lecture 31

Topic: Pitting Corrosion

* Condition favoring pitting →

- 1) Passivating metal, 2) Cl^- presence, 3) Stagnant situation
- 4) Presence of oxidizers (Fe^{3+}), (Cu^{2+})
- 5) Macroscopic } condition - favoring pitting
Microscopic }

Surface

Rough → pitting	→ Roughness parameter
Smooth → less pitting	

Belt grinder	Mirror like
↓	↓
Higher pitting possibility	Much less pitting

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Now course is Corrosion Failures and Analysis, lecture 31, topic Pitting Corrosion. Now, conditions, let us just mention those previous condition, passivating metal, second is presence of chloride ion, third is stagnant situation, fourth is presence of oxidizers Fe plus 3 copper plus 2 because those are strong oxidizers.

Because, why? Because, they can get reduced quite easily. Now the fifth one, let us look at from the point of macroscopic and microscopic conditions favouring pitting. So, this is why you are talking about conditions favouring pitting, ok.

Now, if we look at macroscopic structure of metal, let us say I have a metal surface, two metal surface. And for your information, you can make iron let us say mild steel 0.2 percent carbon steel that you can make a very shiny and mirror like surface by doing metallographic polishing. What you do? We start with the, let you take a sample, you cut it, and then you grind it on a belt grinder first and then take it to different grades of emery papers or we say that polishing papers.

So, those papers the lower the number higher is basically the particle size there, and then as you go higher and higher number of that particular paper, it makes the scratch much finer and finer. So, that is what we start with the belt grinder, and then gradually we remove the scratch, and then finally, we go to cloth polishing belt, cloth polisher. And that in that cloth polisher we polish it in such a fashion that it becomes scratch free and then it becomes shiny and mirror like.

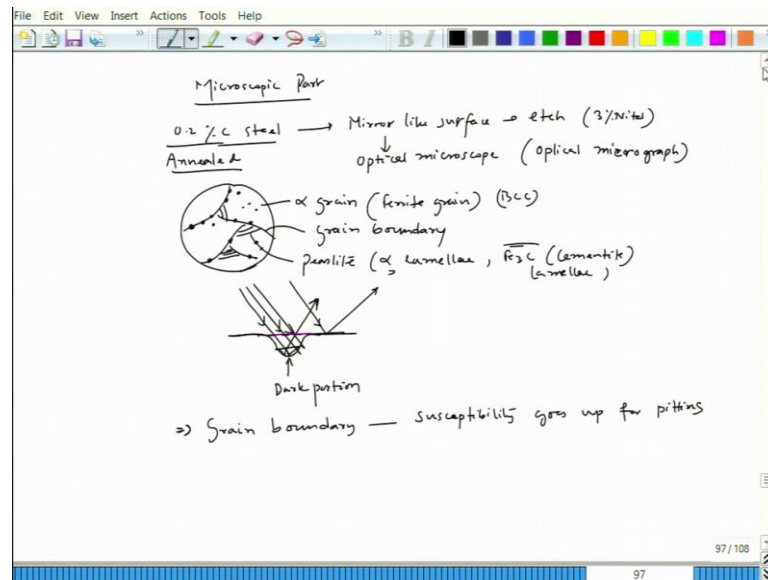
And that mirror like structure, we expose it to etchant to make it etch structure to see the microstructure under optical microscope, ok. So, that way we do metallographic sample preparation. And there if we start with the belt, belt grinder, and let us say it is a mirror like, mirror like structure, ok.

So, in both the cases, this case we have higher pitting possibility, this case higher pitting possibility. This case it will be a much less, much less pitting. The only reason is because that surface is rough, rough surface led to pitting, smooth surface, ok.

So, let us put surface, smooth and rough, less pitting. So, here interestingly we are talking about macroscopic surface, means the morphology or the texture. Remember this texture is not crystallographic texture. This texture is how the surface appears.

For example, you can feel some surface which is rough, feel some surface which is very smooth; that means, it reads to it relates to roughness parameter, ok. So, that rough surface has a much higher pitting tendency, smooth surface has got lower pitting tendency. So, this is on the macroscopic part.

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Now, coming to microscopic part, so in the microscopic part, we mean to say that if we can let us say 0.2 percent carbon steel, if we make a mirror like structure and then we etch it in nital solution, so that means, let us say 0.2 percent carbon steel. We make a mirror like structure surface, then etch in let us say 3 percent nital, and if we look at optical microscope, we will see a structure like this.

So, these are alpha grain which is and here another condition is let us say annealed. That means, it is a very slowly cooled after going to austenite or after austenitization we cool it very slow; that means, in the furnace we keep it and then put up the furnace with the cooling slow cooling of the furnace the sample also gets cooled.

So, that sample we have prepared the optical, we have we have seen the optical microscope. Under my optical microscope optical micrograph, we see, we say that optical micrograph, ok. So, there these are the ferrite grain or alpha grain. So, these are the grain boundary, fine. And, since its 0.2 percent carbon steel, there will be some amount of pearlite. So, those pearlites are presents, very small amount of lamellar structure of pearlite can be visible, so this is pearlite fine.

So, now, this structure, so this is microscopic in nature, until unless we see it under optical microscope, we will not be able to see this structure. Even if you etch it if you want to see with the naked eye, it is impossible to see the structure.

So, this is called microstructure, ok. So, the grain structure, create the structure within this particular system and there are also there is also one more structure called crystal structure. The crystal structure is basically alpha grain if you consider its BCC structure body centered tetra, body, body centered cubic, ok where carbon is present in the tetrahedron position, ok. So, or octahedral position depending on the size of that particular voids.

Now, the carbon is actually sitting in interstitial position, rather, I would better say this. And grain boundary is basically, two grain, the growing grains are actually merging at one point. So, that creates a grain boundary. And pearlite contains alpha, lamella, lamellae, and cementite lamellae.

This is called cementite. So, these are the lamella structures. So, this here again this is BCC, but this is complex crystal structure, it has a complex crystal structure. So, the crystal structure is different, the microstructure is different. Microstructure what we see?

This is the microstructure. Now, here interesting part is when we have this structure, if we try to see the pitting possibility, pitting is more along the grain boundary. Along the grain boundary pitting would be more. And also, the grain body there could be some pits, but those pits would be very few and they would lie close to that particular grain boundary region.

Now if it is deformed that case within the grain body you can find lot of pits. If it is etched, if it is exposed to if exposed to sodium chloride solution, fine. So, this now why do you have lot of pits along the grain boundary? Because, the grain boundary is the active region, because it has a structure which is very active.

Because it the reactivity to the etchant or the chemicals, would be very fast. And interestingly, that is what we would be able to see the grain boundary first, and then we see little bit of features of the grain body.

Now, we have explained that within the grain body grain boundary, there is a dip. So, if we see cross section of the grain boundary, we will see like this, this is the grain boundary. So, then grain boundary, if I try to look at through optical microscope, though those lights are falling here, lights are falling. So, there could be multiple reflection.

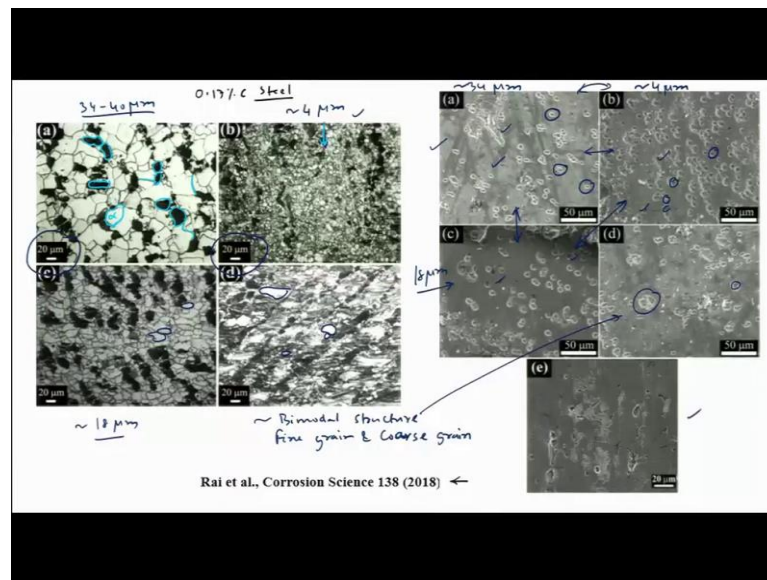
And then finally, the light is coming to the eyepiece and that since there is a multiple reflection along in the particular group that is form along the grain boundary, due to higher reactivity of that particular grain boundary to the chemical, which one is used for etchant for etching that particular surface.

So, that is what because lot of internal reflection, the light energy would reduce. So, that is what this portion would look like dark portion. But the flat section which is the grain body, the ferrite grain, light is coming and then coming to the eyepiece, ok.

So, then you could see that it becomes very shiny. So, that is what grain body looks bright colour, but grain boundary looks dark colour. So, this is the reason. Why? Initially, everything was flat, everything was flat, initially everything was flat.

Because of the reactivity of that grain boundary, it has form a valley there and that creates a situation which allows that grain boundary to get visible to be to grain boundary to be visible, ok. So, now, whether this is experimentally possible, let us see that. So, I have some picture, ok.

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So, let me show those pictures. If we see this particular set of microstructures, now these are all SEM microstructures, remember. And here if you see this is 0 point this is the steel is 0.17 percent carbon steel with little bit of manganese and silicon. And if you anybody wants to check those particular figures, they can refer to this particular paper. So, this is also a work done at IIT, Kanpur.

Now, what has been done here? That particular steel was deformed and recrystallized. Now, in the beginning the assuasive structure had this particular microstructure. So, there, if we carefully see, these are the basically pearlite colonies. You cannot say pearlite phase because it has two constituents, ferrite and cementite. So, that is what we call it called pearlite colony. So, these are the pearlite colonies.

And those white portions are covered by a boundary, so these are the grain boundary, these are the grain boundary, these are the grain boundary, fine, and this is the grain body, this is ferrite, alpha grain, ok. So, this microstructure is as received 0.17 percent carbon, so this is little rolled and air cooled, ok. So, that is the microstructure we get.

Now, in this case the grain size was, one can make out the grain size by looking at this particular micron bar. So, it is around close to 34 to 40 micrometer grain size,

ok. Now, that particular steel was deformed, and after deformation we this particular deformed steel was recrystallized.

Due to recrystallization at some specific temperature and time, very fine microstructure was created. So, that microstructure, so in this particular microstructure this microstructure, so this is the microstructure, this microstructure has a grain size 4, around 4 micrometer, ok.

If you look at this particular micron bar, you could say that the 4 micrometer. Now, after that it was recrystallized for a longer duration at a higher temperature then we created another structure which is having grain size around 18 micrometer, ok. So, if you see the grain size is much smaller. So, these are the grain size, ok. So, these are the you know which is around close to 18, my average grain size is 18 micrometer.

Now, after that we also created some condition, we have used, we have created a bimodal structure, where fine grain and coarse grain microstructure is created, ok. So, now, you can see that some grains are quite large and some grains are very small, ok. For example, these are the small grains, these are the small grains, and one grain is very large, ok. So, like that large grain and small grain that particular microstructure has been created.

Now, this particular steel was exposed to 3.5 percent NaCl solution, ok. And once it is exposed to 3.5 percent NaCl solution, we could see that the surface contains pits, so these are the pits. Now, this is the steel corresponding to as received one, which is having grain size around 34 micrometer. Now, as the grain size decreases due to recrystallization which is this one, so this one is 4 micrometer grain size. So, there pits, number of pits have gone up.

So, these are the pits, and you see the number of pits if you compare between these two the finer grains, have got much higher pit. Now, once we increase the grain size to 18 micrometer, we see the number of pits have reduced compared to this, but it is still larger.

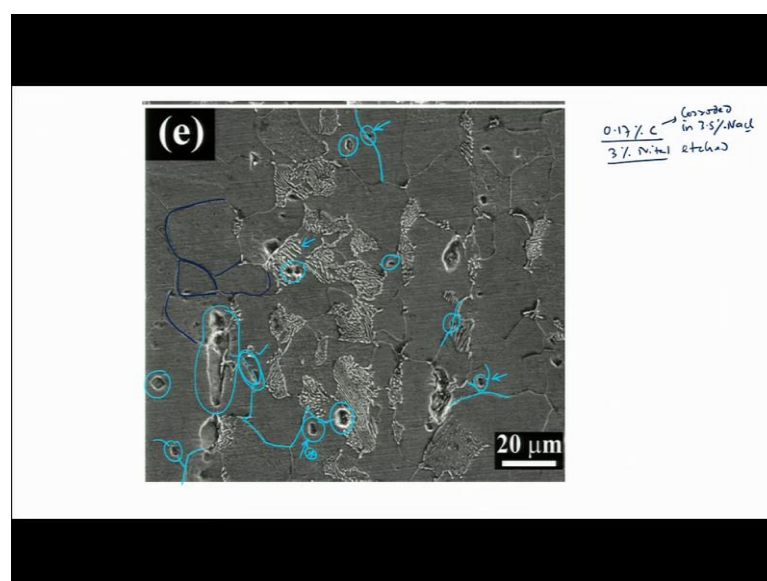
If we compare this two and if you compare this two, this is in between the, its grain size is in between this two, one is 34, one is 4 micrometer, and here it is 18 micrometer, which is let us say 18 micrometer, ok.

So, now, number of pits have reduced compared to this one which is 4 micrometer, but it is number of pits is more in this case compared to this. So, now you know interesting part is you could see there is a kind of relation that larger the grain size, lower is the number of pits, and smaller the grain size higher is the number of, larger number would be the pits. And similarly, if we contain bimodal structure, so this is basically the bimodal structure, ok.

So, their number of pits are also there, but those pits are some pits are much larger than these two cases. So, this case and this case if you compare, this case some pits have gone very large, ok. But now, that means, if we reduce the grain size, the number of grain boundaries or the amount of grain boundary, volume fraction of grain boundary will go up. Since, the grain boundary is the active zone, so the possibility of pitting would go up. So, that is what it exactly happened.

Now we have to also see whether those pits because here it is not clear where those pits are formed. In order to do that, this particular steel after formation of pit we remove the top layer, and after removing the top layer we etched it. And once we etched it, we could see that the some of the pits which have gone little deeper into the material those left their impression on that particular microstructure, ok. So, this is that microstructure. So, let me show to the zoom version of that microstructure.

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This is the zoom version of that microstructure. So, this is 0.17 percent carbon, weight percent of course, and this is etched in 3 percent nital. And before that, it was corroded in 3.5 percent NaCl. Please go to that particular paper, and you can see all the conditions over there.

Now, after etching of that corroded surface, after carefully removing the top corroded surface, we could see the grains again. So, these are the grains, these are the grains, is not it. So, and pearlite is also visible, so these are the pearlites; these are the pearlites, so these are the pearlites.

Now, interesting part is we could also see pits, so these are the pits. This is a big pit, this is a small, another pit, this is another pit, and there could be pit like this small pit. So, the pit has also gone inside the pearlite colony. And this pit has formed just between the boundary and boundary between ferrite grain and pearlite colony, so there it has formed.

Now, interesting part is this pit if you see, this pit is also there. Now, interesting observation, if I consider this pit, this is the grain boundary you see. This is the grain boundary. And the pit is actually going, and if we draw those particular grain boundary, so it actually on the grain boundary.

Similarly, here if you see this one, this is the grain boundary, and the pit is forming on the grain boundary. Similarly, if we see this one, so this is the grain boundary between or the interface between ferrite grain and pearlite colony is a there is a pit.

Now, if we see another, this is the grain boundary, and the pit is exactly on top of grain boundary. Now, mostly most of the pits are actually happening on the grain boundary. There are some pits which are actually forming within the grain. So, this is also on the grain boundary. So, the grain boundary you can plot. So, this is the grain boundary, this is another grain boundary. So, this has formed on the grain boundary.

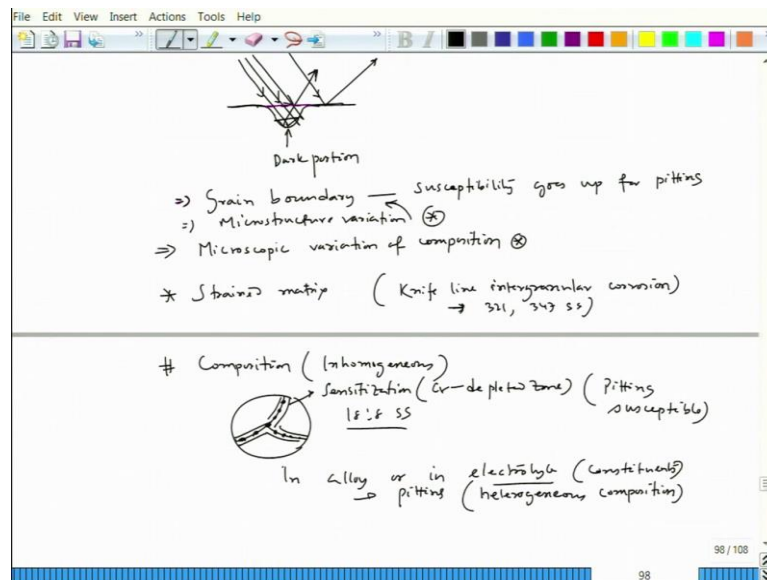
Now, some pits for example, if I look at this pit. This pit has formed within the grain body, but interestingly, it is not at the center. This is the center of the grain, so this has formed close to the grain boundary. So, this is the grain boundary and this is the pearlite ferrite colony interface, this has formed close to that particular boundary.

Even if you consider this one, this is the grain boundary, this is the grain boundary, but it has formed close to that. So, that means, the grain boundary regions are susceptible for pitting, ok. One is, and that is what if we increase the number of grain boundary or the amount of grain boundary, you would definitely increase the pitting possibilities along the grain boundary or number of pits would also go up.

Similar thing has happened here, 34 micron to 4 micrometer number of pits have gone up. 4 micrometer to 18 micrometer, the number of pit has reduced to a extent. So, that is what is the impression of grain boundary on the pitting possibility. So, coming back to our page, so that means, the grain boundary, the microstructure plays a big part in giving you pits and the grain boundary is the one of the susceptible areas for pit. So, now, we can say that susceptibility goes up for pitting.

So, one small study we have done, and then that clearly indicates that why it happens. Now, microscopic change in the metal, one is definitely microscope microscopic features.

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Now, microscopically there is one more involved thing which can involve there, that is microscopic variation of composition. See, one is microscopic variation of microstructure, microstructure variation, another one is microscopic variation of composition. The microscopic variation we have talked about grain boundary, is not

it. There could be variations like which is a combine effect with composition and microstructure variations.

For example, let us say, if it particular structure is strained, strained matrix, ok. So, if we recall one particular situation where we talked about knife line attack, which happens in the stabilized steel which is let us say 321 or 347. So, this kind of stainless steel one can have knife line inter granular corrosion.

So, that time what we observed that steel after doing we have to do solutionization treatment, and that solutionization treatment we do it at around close to around 1200 degree Celsius.

And there, what happens? Everything goes into solution, all those niobium carbide or titanium carbide they also dissolve, and chromium carbide also dissolve, and then it becomes homogenized microstructure, homogenized structure, ok composition wise. So, then, that steel would have a higher resistance to knife line attack or grain boundary attack.

But thing is if that particular steel is deformed, and then taken to again to around 800, 500 to 800 degree Celsius after doing solutionization treatment, homogenization treatment, the entire steel becomes susceptible to inter granular corrosion and that particular steel everywhere one can have pitting. So, that means, strained matrix which is also creating a kind of microstructural variation in the steel and that strained one, we have to relieve the strain in order to avoid stress related issues.

So, that during that stress relieve operation if we take it to around 500 to 800 degree Celsius, since there are no titanium carbide or chromium carbide its absolutely, fine. But once we take it to there because of the stress relieve operation, entire steel we have chromium carbide, because the niobium carbide or titanium carbide cannot form. For the formation of niobium carbide titanium carbide, one has to take it to around 1000 degree Celsius.

Since, it is not taken there only chromium carbide comes out and that creates a situation that steel would be very susceptible to inter-granular corrosion as well as pitting corrosion. So, that means, the strained matrix is also a reason for pitting

corrosion. But if I talk about composition, now composition creates huge issue. We talk about homogeneous, inhomogeneous composition, inhomogeneity. Now, what happens?

For example, if we have a stainless steel 18 8, 18 8 stainless steel, this is the grain boundary, because of chromium carbide precipitation, after sensitization, fine, this can happen during welding in that weld decay zone. So, those zone we have the surrounding areas, along the grain boundary, we have a situation like sensitization or chromium depleted zone. And we know around 12 percent weight percent chromium is needed for giving stainless steel property, stainless property.

Because the chromium beyond 12 percent it actually passivates quickly forming chromium oxide passive layer, and that leads to passivation, fine. So, since the chromium depleted zone that forms due to the chromium carbide precipitation along the grain boundary that chromium depleted zone would be susceptible to pitting. So, this zone would be pitting susceptible.

So, that means, it is a compositional inhomogeneity leading to pitting. So, the compositional inhomogeneity can lead to pitting in, several such examples are there. For example, in case of 5083 alloy which is aluminium magnesium alloy. So, there also, this compositional inhomogenization because of the beta phase formation precipitation, one can have compositional inhomogeneity along the grain boundary. And then those precipitates, those are actually active precipitates, those dissolve and then create pits.

So, it is a highly pit prone metal, or pit prone aluminium alloy, ok because of that beta phase precipitation along the grain boundary. So, compositional inhomogeneity can also happen in case of stainless steel. For example, if we have sulphur in it, if we have manganese in it, the manganese sulphur can combine and form MnS. And MnS can also combine little bit of chromium. So, then that inclusion that happens, those inclusions are active inclusions.

Those inclusions can dissolve and leave a pit over there, on the microstructure, on the surface of that particular metal. So, the composition inhomogeneity can also lead to serious pitting in many of the circumstances, whether it is a passivating metal or

non-passivating metal, does not matter. Those, compositional inhomogeneity, can create problem regarding pitting fine.

So, composition inhomogeneity in the metal there could be compositional inhomogeneity in the solution. For example, chromium content can be little high at one location sorry not chromium content, chloride content could be high at one location chloride content could be low at one location of that same metal surface fine. So, the where the chloride content is little high that portion would be susceptible to pitting.

So, those kind of stuff that composition inhomogeneity on metal, in the metal or alloy or in electrolyte constituents. So, those can lead to pitting, pitting due to heterogeneous composition. In metal or alloy, not metal I would say, it is it should be in alloy or in electrolyte, we can have pitting because of the inhomogeneous composition across the surface. It can be provided, it can be possible in the alloy surface or it can be possible in the solution.

So, those are the situations can lead to pitting. So, these are in general, these are the kind of conditions can that can lead to pitting. So, let us stop here on the condition part. Now, next lecture we will talk about mechanism part and then some of the protection routes what we can have to prevent pitting. So, let me stop here.

Thank you.