Corrosion Failures and Analysis
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Lecture - 18
Graphite corrosion and protection from dezincification

Welcome back to the Corrosion Failures and Analysis. Today, we have lecture 18 and our discussion point will be today we will conclude the discussion on dealloying or selective leaching. And, then will begin discussion on another corrosion form, which is called intergranular corrosion.

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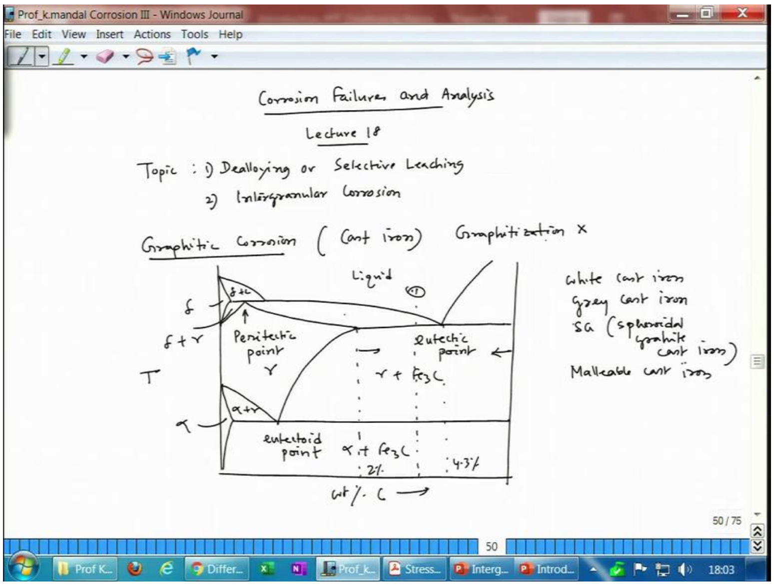

Corrosion Failures and Analysis

Lecture 18

Topic : 1) Dealloying or Selective Leaching
2) Intergranular Corrosion

Graphitic Corrosion (Cast iron) Graphitization ×

White cast iron
Grey cast iron
SG (spheroidal graphite cast iron)
Malleable cast iron

So, course is called ok. So, and the second topic will start today is intergranular corrosion. Now, if you recall our previous lecture 17, we started talking about some of the examples, what we have seen in case of silver cop silver zinc system, we have seen the example in case of nickel zinc system.

In case of silver zinc system we could get pure silver network starting from very lean silver containing a silver lean composition silver 25, zinc 75 alloy composition. And, similarly we have seen formation of zinc oxide nano rods on top of nickel core, by doing dealloying of nickel zinc alloy ok. That alloy was made by powder metallurgy root which is ball milling and mechanical alloying starting with a elemental powder nickel and zinc.

And, then we de alloyed in 0.5 mole normal NAOH solution fine. And, we could get zinc oxide nano rods on top of nickel core. So, and then we will started looking at dealloying in other systems. So, one system is such in steel, which is very popular system, here we could see that in case of a 100 percent pearlite microstructure.

We could make, we could separate out cementite plates by doing forceful polarization where dealloying of pure iron or ferrite takes place, and goes into the solution leaving behind cementite. So, here though it this is not a typical of pure elements, rather one element is pure almost a pure form, but other cementite which is basically a compound, we can be considered as a single melting point compound.

So, we can assume to be a kind of single entity or single since it is a basically stoichiometric compound fine. So, their cementite stays back and ferrite goes out. Similarly, in case of spheroidal iron, where spheroids of cementite stays back and iron goes out in the form of iron ions into the solution.

So, that their de alloying takes place in the ferrite ok, the ferrite goes out. And, both the examples I could cite for because we have worked on that particular field in the lab ok. So, this is a typical example of galvanic corrosion, but that galvanic corrosion leads to a selective dissolution, here you can say that is selective leaching.

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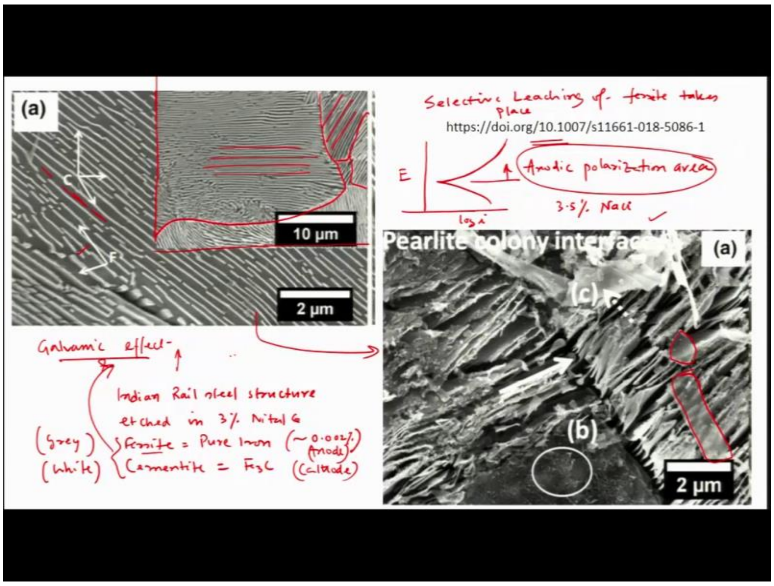

Selective Leaching of ferrite takes place

https://doi.org/10.1007/s11661-018-5086-1

Anodic polarization area

3.5% NaCl

Galvanic effect

Indian Rail steel structure etched in 3% Nital 6

(Grey) Ferrite = Pure Iron (~0.002%) (Anode)

(White) Cementite = Fe_3C (Cathode)

So, let us get back to that particular example for example, here. So, the selective leaching of selective leaching of ferrite takes place, or dealloying of ferrite takes place.

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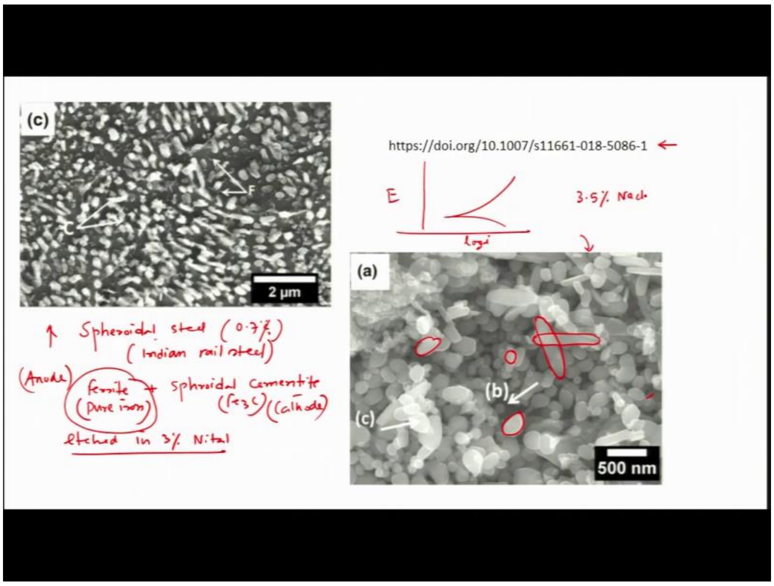

https://doi.org/10.1007/s11661-018-5086-1 ←

3.5% NaCl

↑ Spheroidal steel (0.7%)
(Indian rail steel)

(Anode) (ferrite (Pure iron)) + spheroidal cementite (Fe_3C) (cathode)

etched in 3% Nital

Similarly, another example we saw in case of spheroidal steel where initially it was politic steel and then it was converted to spheroids by doing heat treatment, which is called a spheroidal heat treatment. And, then we could see that preferential dissolution of a iron or ferrite leaves behind the spheroids of free standing sparoids of cementite ok.

So, this is these are the examples. So, please go back and look at the look at lecture 17 to understand these two pictures. So, now another picture and this is the reference if you want to see that reference if this is the reference, which is basically work we have done at IIT Kanpur fine.

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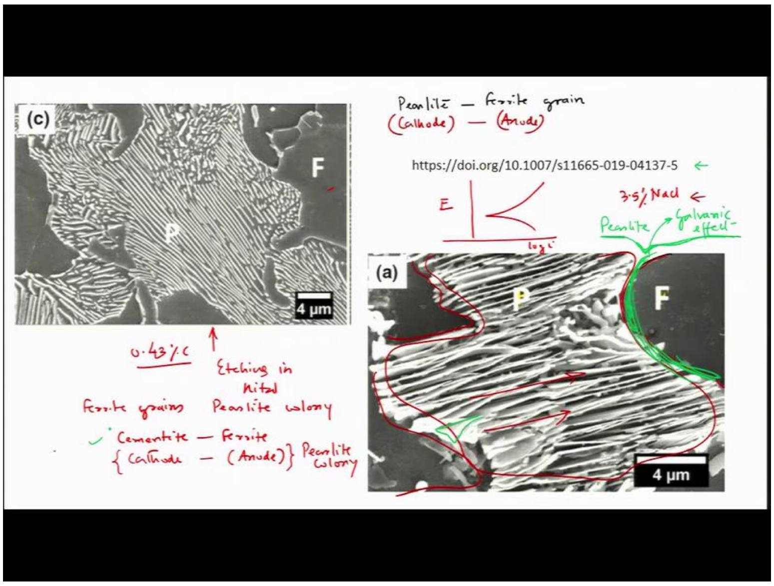

https://doi.org/10.1007/s11665-019-04137-5

Now, this is another example where 0.43 percent the carbon content is 0.43 percent carbon. So, there we have ferrite as well as pearlite. So, this is the ferrite part this is the pearlite and this is this microstructure is obtained by etching in nital fine. Now, there we have two phases; one it one is ferrite grains, another one is a pearlite colony.

See pearlite cannot be mentioned as a phase, because it is a phase mixture we have both the phases, one is cementite, one is ferrite. So, that is what it is called pearlitic pearlitic colony. Now, this ferrite grain and pearlite colony, this particular microstructure we develop by nital etching.

But, now if we start with (Refer Time: 06: 23) sample polish and (Refer Time: 06: 25) sample, that if we do again a polarization. So, again the polarization is done and those polarizations are done in NaCl solution, 3.5 percent NaCl solution. And in fact, here also it is done this polarization is done 3.5 weight percent NaCl solution. Similarly, this is also done in 3.5 percent NaCl solution ok. And, this is freely aerated; that means, it is exposed to open atmosphere.

Now, here why I am showing this picture, this actually also combines both the galvanic effect as well as the alloy. Let us see that, that is what I thought that let us let me discuss this particular picture. Now, this is a micrograph which is developed after polarization. So, this is a kind of polarization we got at a very high value of polarization we got ok, to the anodic part and after that we took the microstructure. Remember after polarization we have not done any etching, this particular picture has formed due to selective dissolution of ferrite ok.

Now, interestingly cementite is all the time, cementite and ferrite this couple is considered, if this couple is considered, then this will act as anode, and this will act as cathode. This happens in this particular situation happens in case of pearlite colony ok.

Now, if you take pearlite and and ferrite grain. So, this is one grain, this is one grain of ferrite. This is another grain of ferrite, this is another grain of ferrite or we call it alpha iron and this is the pearlite colony. So, this part is basically pearlite colony. And, this is you can say that this is almost a single pearlite colony, because all the laminar orientation is similar in one direction; all are in this direction ok. So, that is why it is a single colony.

Now, in the pearlite colony we have ferrite lamella and ferrite cementite lamella. So, the cementite acts as cathode and ferrite acts as anode. But, when we talk about ferrite grain and pearlite colony, pearlite colony since it has a lot of cementite and cementite is cathodic in nature, overall it will act as a cathode and this is anode. And, now anode would dissolve as per the galvanic effect in this particular solution.

Now, question is when this dissolves, the dissolution effect will be seen adjacent to where does this pearlite and anode pearlite and ferrite grains are in contacts. So, the dissolution pattern will be seen around this zone, around this zone. In fact, we have seen this particular effect by doing AFM image, where it is very clear, that if we see the depth profile, here the depth is very high and then it will become like this.

So, the pearlite this is the pearlite depth and this is in the contact point region, the depth has gone back this is on the same level, but in that area where pearlite colony and ferrite grains are in contact, there we have good amount of the dissolution has happened quite a good distance. And, then gradually the distance has gone up and then finally, the ferrite grain again becomes almost of the same level as pearlite level. Because, here we have in this particular region we have galvanic effect.

It also relates to the point that we talked about in galvanic corrosion that contact point is the most vulnerable region, where corrosion of ferrite have corrosion of active metal happens at a rapid rate, compared to the place little away from the galvanic contact point. So, this is the galvanic contact point where pearlite colony acts as cathode and ferrite grain acts as anode. So, that is what you have dissolution of ferrite close to that contact.

And, then as you go away from the contact point the dissolution depth decreases gradually. And, finally, it becomes almost of the same level as the pearlite level ok. So; that means, this is that is what I wanted to bring in this particular picture. Again if you want to see this particular paper you can see this is also our work. Now, this happens between pearlite colony and ferrite grain, but in the pearlite colony we have selective dissolution of those ferrite lamella, leaving behind standalone cementite.

You would see that the cementite this cementite you see this is a kind of cementite plate, that cementite plate has bent because gradually you are taking away ferrite in the form of iron ions into the solution, leaving behind those cementite plates standalone cementite plates. That happens because of this effect ok. Where cementite lamellae acts as cathode, ferrite lamellae acts as anode and the anode dissolution takes place and here anode is nothing but almost your iron ok.

So, this is a kind of mixed is a combination of de alloying in the pearlite and galvanic effect between pearlite colony and ferrite. So, this is a classic combination react combination modes combination mode ok. So, now let me talk about, let me talk about graphitization ok. So, this is an example let us put or we will call it graphitic corrosion. So, this happens in cast iron. So, some book it is written as graphitization ok.

So, this I think this is my personal opinion that this should not be used, while talking about corrosion of cast iron ok. Graphitization means, formation of graphite during cooling stage of a cast iron ok. So, that time if we see iron carbon phase diagram, this is a semantic picture you can say I am not putting all those specific values, but in semantically it is a basically this is called peritectic ok.

So, this is eutectoid and this is eutectic points. And, these are different phases are this is liquid iron, this is delta plus liquid, this is delta region, this is delta plus gamma, this is gamma, this is alpha region, this is alpha plus gamma, this is alpha plus Fe_3C, and here we have gamma plus Fe_3C ok.

And, this is weight percent, of carbon fine. And, this is temperature you can go to some of the books usual physical metallurgy book you will get this diagram. Now, up to this point we call it this is around 2 percent and this is 4.3 percent carbon ok. So, this 4.3 percent carbon so, between this to this we have cast iron zone. And, there from here let us say you are here ok.

So, from there if you do a slow cooling depending on the cooling rate, either you get cementite austenite, if you do a slow cooling you will get graphite ferrite and if you have a little higher cooling, you can get graphite as well as pearlite. So, those are the kind of micro structures you will get, but one such microstructure. So, there are different steels called different cast irons, white cast iron, grey cast iron, then SG cast iron, spheroidal graphite cast iron, then we have malleable cast iron.

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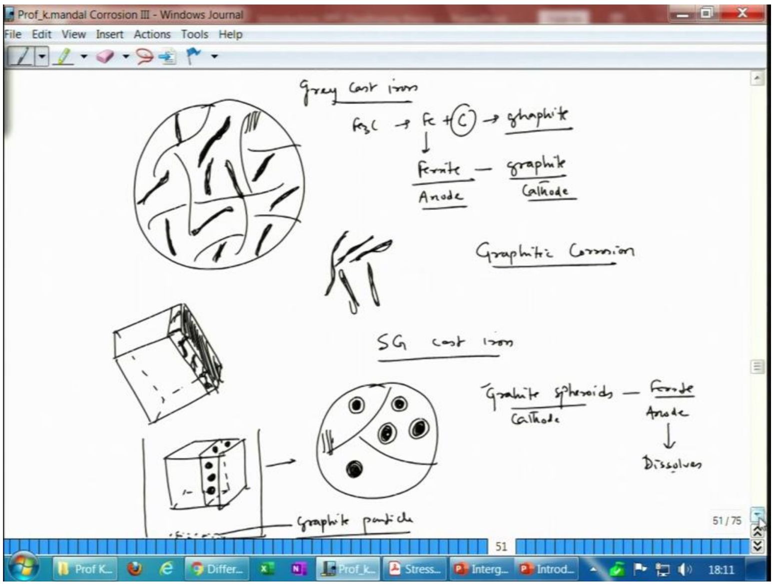

Now, if I see the cast iron that is forming in case of grey cast iron, if it is the ferritic grey cast iron or pearlitic grey cast iron. So, microstructure could be you have those grains, ferrite grains or there could be a possibility of pearlite ok. Some pearlite presence should be there and these graphites are actually basically in the form of flex. So, these are graphites, these are the graphites, these are in the flake form.

Here what happens? Cementite breaks and then form iron and so, this is cementite Fe_3C breaks and form iron plus carbon and this carbon is nothing but graphite ok. Now, here also there could be a possibility of preferential dissolution of ferrite which is nothing but ferrite.

And, the ferrite can dissolve leaving behind graphite in the matrix ok. So, now, if the ferrite dissolve, because in this particular case this acts as anode, this acts as cathode fine. So, this anode cathode; that means, anode should dissolve cathode would stay back. Since, the graphite is actually basically having a kind of flaky arrangement and once the one layer of iron dissolves, this graphite can have interlocking between them.

So, if you see from a cross section point of view, this cross section. So, if you see this part. So, this part there would be individual graphites. So, these graphites will have interlocking between them, the top surface if you see a polished grey cast iron, this is a grey cast iron.

So, it will look shiny ok. Though there would be if you compare with the steel polish surface, scratch less polish surface and grey cast and scratch less polish surface. In the grey cast iron polish surface, you might see a little bit of greyish nature not very shining as you see in case of steel case, in case of carbon steel, because of the graphite presence fine.

Now, if you start with that polished surface. The shiny nature is almost lost and the surface would become very much grey colour ok. And, that grey colour, if you take this surface and then rub on a white paper, it just gives you this kind of appearance or the mark, which should you should get by having a pencil rubbing against a white paper. So, this is nothing but the graphite ok.

Now, if you take a spheroidal cast iron SG cast iron. So, there this similar effect can happen. So, there the microstructure is so, these are let us say a ferritic matrix or little bit of pearlite is also there. There the graphites are in the form of spheroids. And, interestingly around that spheroid if it is a pearlitic SG iron, then you will see that around that there is a white layer, the white layer.

And, those white layers are nothing, but a pure iron or ferrite, because while graphite forms surrounding that area it actually takes a takes carbon and forms graphite ok. That cementite breaks and then that is what that around that area becomes whitish. So, that is not our discussion point, but, now if we have the dealloying in this case where the similar this graphite, spheroids and ferrite.

This one and this one it will act as anode and it will act as cathode since in the galvanic series this is having higher potential in a solution in a normal solution or acid solution this will be acting as a cathode. So, now, there this dissolves preferentially, because of the galvanic effect and then leaving behind graphite spheroids ok.

So, but since these are not interconnected here if you see it is basically if you see under three dimensional picture. So, let us say this is the layer I am talking about, this is the layer I am talking about the spheroids are actually not having any interconnection.

So, because of not having any interconnection as the layer disappears due to dealloying or the ferrite dissolution, this graphite those graphite spheroids will fall off from the surface. And, it will if you do it in a beaker, if you do it in a beaker, you will see that the bottom some small, small black stuff stuffs have collected have been collected ok.

So, this collection of black stuff you will see so these are nothing but graphite particles. And, this happens because during this case those spheroids are not having interlocking. So, that is what they it is very easy to fall off rather than in case of graphitic case, where in case of grey cast iron where graphites are flaky.

So, that is what they have interconnection so they do not like to leave the surface, so, but mechanism wise both the same. So, this is one particular corrosion mode which you will call it graphitic corrosion. So, this is also falling under dealloying process.

But, here you see interestingly in case of zinc copper system. We could see that copper redeposit’s back in case of silver causing system silver deposits back. In case of you can go to the literature and search silver copper silver system ok. In case sorry in case of copper gold silver system, silver dissolves gold stays back. So, that is what you have fantastic network of pure gold porous structure ok.

So, there what happens? Both dissolves first and then, pure this noble metal deposits back. In case of copper zinc copper deposits back, in case of silver zinc silver deposits back. So, there we see that the preferentially both dissolves and then one pure one noble metal noble ion deposits back.

But, in this case we do not have dissolution of both rather one dissolves and the second one is left behind. So, in this graphitic iron or in the steel corrosion what we have seen, there the mechanism the first mechanism which says that, active metal dissolves and the noble stuff stays back, that particular concept is valid here.

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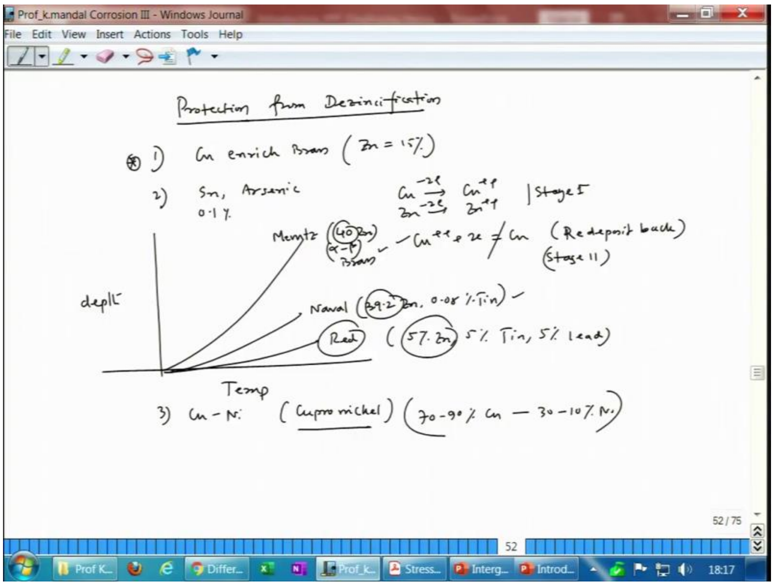

Protection from Dezincification

1) Cu enrich Brass (Zn = 15%)

2) Sn, Arsenic 0.1%

$Cu \xrightarrow{-2e} Cu^{++}$ | Stage I

$Zn \xrightarrow{-2e} Zn^{++}$

Muntz (40 Zn) ($\alpha-\beta$ Brass) $Cu^{++} + 2e \not\rightarrow Cu$ (Redeposit back) (Stage II)

Naval (39.2 Zn, 0.08% Tin)

Red (5% Zn, 5% Tin, 5% lead)

3) Cu - Ni (Cupro nickel) (70-90% Cu — 30-10% Ni)

Now, coming to some of the protections what we can have. In case of zinc brass system, we can use protection from dezincification; protection from dezincification. One is we can have copper envy, copper enrich brush say a zinc could be around 15 percent we can reduce dealloying to a great extent.

Second we can add little bit of tin or arsenic ok. Arsenic so, what it does around 0.1 percent or around close to 1 percent arsenic if you would add there. They actually deposits back and then prevent redeposition of copper iron, though first layer dissolves, but after that silver arsenic redeposits back. So, that it does not allow copper to redeposit back. So, one step is broken.

So, whenever we have a step reaction. So, what happens here the step reactions happen, copper zinc dissolves fine and then copper redeposits back. So, the next step this is stage 1, second stage is copper plus plus plus 2 electron minus 2e minus 2e it deposits back redeposits back. So, this is you can say stage 2.

So, now if this is broken, then the first step cannot go on ok. So, that time and of course, that time zinc stays there in the solution and we have dezincification. But, this arsenic what it does? It forms a layer on top of copper zinc alloy and then it does not allow the secondary second stage to happen. So, that is what it is protected ok.

We can have for example, one such diagram of and coming to this particular effect, one can see the study that temperature and depth ok. So, some of the metals that for example, muntz metal which has around 40 percent zinc, then one can have which is alpha beta brass. So, then one can have naval branch which is around 39.2 percent zinc and 0.08 percent tin. So, I said that this is around 0.1 percent addition ok. And, then red brass which is around 5 percent zinc, 5 percent tin, and then 5 percent lead.

So, this one if you see as the temperature increases, the depth of attack or the depth of dezincification is very low in case of raging. Because, here the zinc is very low 5 percent rest of the thing is copper all the cases fine. So, that is the advantage of having even in case of for example, if you compare these two only little bit of this is tin ok.

Only little bit of addition of tin has prevented the dezincification to a great extent ok. Because, you see here it was 40 percent zinc and here 39.2 the rest of the thing is copper and 0.08 percent tin, which is 0.1 percent tin. So, it prevents the dezincification fine.

So, that is another protection and then another route is in case if you have a very aggressive solution, it is better not to use brass rather than use a copper nickel system ok. So, their cupronickel can be utilized this is called cupronickel or cupronickel. So, this is cupronickel which is close to 70 to 90 percent copper and rest is nickel 30 to 10 percent nickel.

So, this is an alloy one can use in case of aggressive solution where dezincification cannot be avoided. So, these are some of the protection routes one can use ok. So, let me end the dezincification, because I have given lot of examples, examples from the lab examples from the from actual practical situation, where the brass pipe example we have talked about. We will talk about intergranular corrosion from the next lecture onwards.

Thank you.