Corrosion Failures and Analysis
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Lecture - 15
Dealloying/Selective leaching

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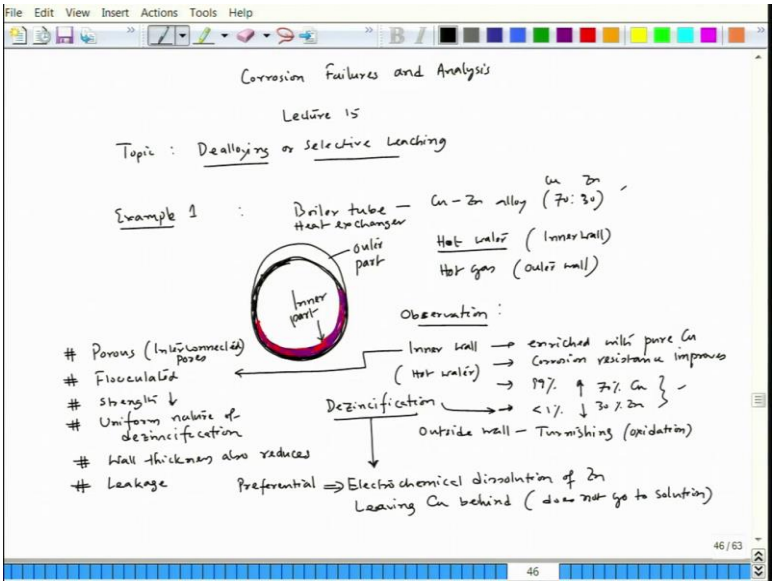

Welcome to the course corrosion failures and analysis, we have a lecture 15 and the topic will be Dealloying or Selective Leaching. Now, as the name suggest that it is just opposite of dealloying. In case of alloying what we do? We mix a number of elements and then make solution of it ok. So, that is alloying and dealloying we are actually taking element out of an alloy ok. So, that time it becomes dealloying.

Selective leaching is also like selectively taking one element from an alloy and then that element goes to the solution and, but here one thing is important in case of alloying we can do it via casting route, we can do it via electro deposition route, but in this case specifically it is done via electrochemical route. So, that means, out of let us say a and b that are two elements present in an alloy, we are taking a element out preferentially leaving b element.

So, that the alloy become enriched with b and depleted with a. So, that happens in an electrolyte medium, so that part we will be looking at. Now, the dealloying is basically in many books it has been written as dezincification, denickelification. So, those kind of

names are given, but the general name is dealloying or selective leaching. So, this dezincification is specific to copper zinc alloy system ok.

So, in denickelification is specific to copper nickel alloy system. So, those are the special name given to this. Here also dezincification is basically taking zinc out from copper zinc alloy ok. So, let us look at what are the basic traits of dealloying and we will also try to understand some of the examples as well as try to understand theory and then we will try to look at the protections.

Now, let us say if it is for example, example 1; let us say it is boiler tube which is made of copper zinc alloy fine. So, now, that tube if we take a small sections out of it. So, small segment out of it, it will look like is a small segment.

So, inner part, this is the this is the thickness of the pipe, this black portion and let us say this is the inner part and this is the outer part ok, a small segment here hot water it carries hot water and outside is inner wall and outer wall is hot gas, it is basically a heat exchanger right.

Now, it can be noticed that inner part this inner part notice or observation from a prolonged operation, inner wall enriched with almost pure copper. And of course, if it is a pure copper corrosion resistance improves. So, that means, if it is a brass 70, 30 brass; that means, 70 percent weight percent copper and 30 weight percent zinc. Then what happens? The inner wall the copper content, this inner wall copper content might reach to even 99 percent ok.

So, this is I am just taking that 70, 30 it could be 60, 40 also. So, depending on the requirement, but it is a brass. Now, 99 percent and it has enriched from 70 percent copper and the wall zinc content might reach to less than 1 percent and that has decreased from 30 percent zinc if we consider this.

Now, this is, but outside wall nothing happens. Yes, there will be tarnishing or oxidation, but that such situation does not arise because it happens because it carries hot water. Now, if we see this situation that enrichment of copper happens. So, that is what this is a typical example and depletion of zinc happens. So, that is what it is given a name dezincification and this is basically related to depletion of zinc and interestingly here this dezincification happens over the, across the entire inner wall.

So, inner wall it would become red colored because the copper has a red color from a bit of orange color what is there for copper zinc alloy. Now, this we can put a red tint here rather let us put. It will not be like a red colored ok because of the copper pure copper. But if we analyze this inner wall, this inner wall further; analyze the inner wall further, we will see that this inner wall actually though its corrosion resistance has improved it is porous; second thing is it is porous it is flocculated.

And if we do a mechanical property its strength also would reduce strength also would reduce and interestingly if we look at very carefully it is interconnected porosity interconnected pores. So, now, sometimes there could be possibility that this particular thing and interestingly if we see that this is happening over the entire inner wall and it is more or less uniform. So, that is what we can say that is another observation, uniform nature of dezincification right.

So, this is one such example that copper enriches and zinc depletes and that is what we give the name of dezincification. Now, it might happened another observation that inner wall it become slow flocculated and porous the wall thickness can also reduce. Why? Because of the pressure of the hot water that might lead to blowing this particular porous flocculated layer might get blown away and we can get wall thickness reduction ok. So, and now question is let us say it is 1 plus some local places wall thickness has reduced.

So, there again this particular phenomena would happen and so likely there could be a kind of leakage ok, so that is also possible. Now, see this reduction of zinc or the depletion of zinc happens after that the analysis has been done and then it was realized that this dezincification happens due to electrochemical dissolution of zinc ok.

And that to preference or I would say preferential dissolution; preferential electrochemical dissolution and copper sorry, resolution. So, here a leaving copper behind. So, that means, copper does not go to solution; does not go to solution fine.

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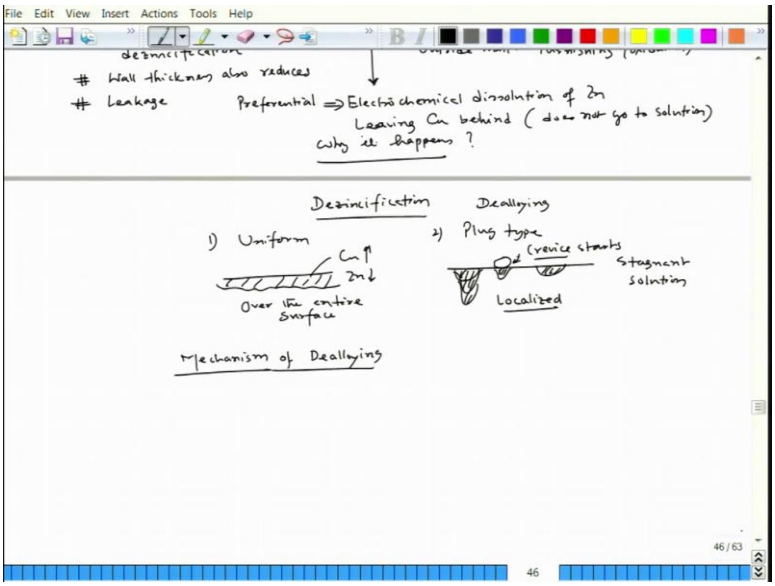

Now, question is we have to look at why this thing happens, that part tells us the mechanism of in order to know that we have to understand the mechanism of the alloy. Now, interesting part is here we could see that this wall, this dezincification is happening over the entire wall, but some cases it might happen locally ok, locally it might happen and that case we call it as a plug type dealloying ok.

So, that means, there are two variants or dezincification one is uniform, another one is plug type. In fact, plug type it would be more deter more deteriorating kind of is a basically host compared to these two variants because plug type happens locally. For example, if we have one particular brass. So, that time if it happens uniformly over the entire brass section. So, the here let us say the copper content has enriched zinc content has because the zinc dissolves into the solution, but plug type happens locally like this.

So, here local cases we have this plug type. So, this generally plug type happens wherever there is a stagnant solution. So, this is stagnant solution that plug type things can happen or let us say there is some kind of, let us say kind of object that is falling on that particular brass wall and if it is stagnant. So, there could be possible that the crevice starts and that crevice corrosion would lead to a plug type dezincification ok.

So, these are the two variations of dezincification, so in fact we can say that this is the two variations of dealloying also. So, one is localized one is over the entire surface, another one is very much localized ok. And localized is bad because you know a very

local point since this dezincification is taking place. So, that can might progress in a local mode and there could be possibility that if it is a pipe then it can leak or if it is a wall containing some fluid which is stagnant. So, that can also leak.

So, that is what this is bad type of dealloying plug type ok. Now, coming to the mechanism part, which is the most fascinating. So, people have studied this mechanism of dealloying ok. Before that let us show one example of plug type, this example if you go to Fontana and Greene book Corrosion Engineering in that book you will find this example ok, this for the example I have we have just discussed.

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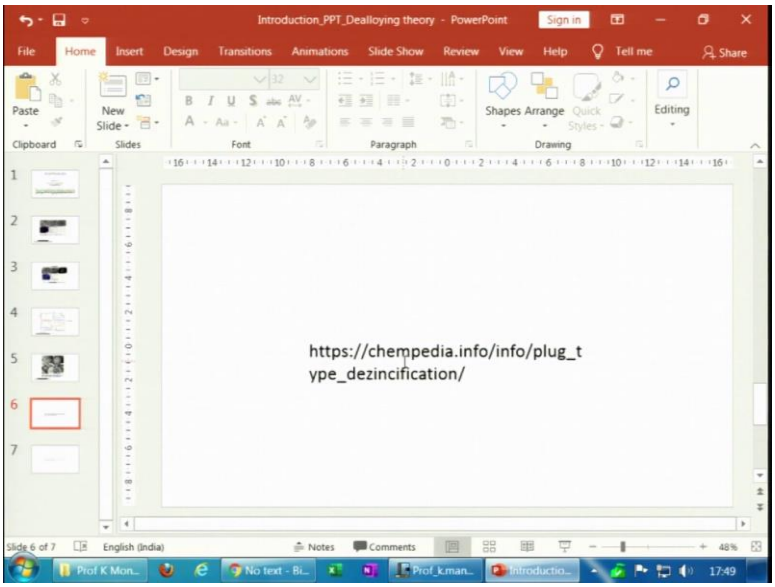

Now, another example I just would like to go to net. Remember this is the website you can go through and then have a look at that picture of dealloying which is a plug type.

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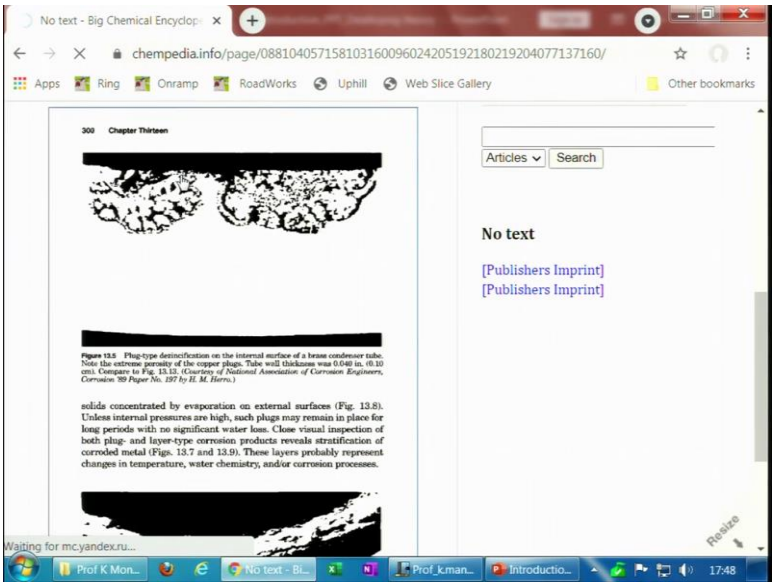

So, here is one classic example of plug type. So, this is a brass condenser tube, you know internal surface of the brass condenser tube that extreme porosity of the copper plug. So, this is basically copper plug. Why they are saying copper plug? Because here in this particular case those are mostly copper porous copper because zinc has gone out of it and that is what those are called copper plug and it is not uniform, it is localized.

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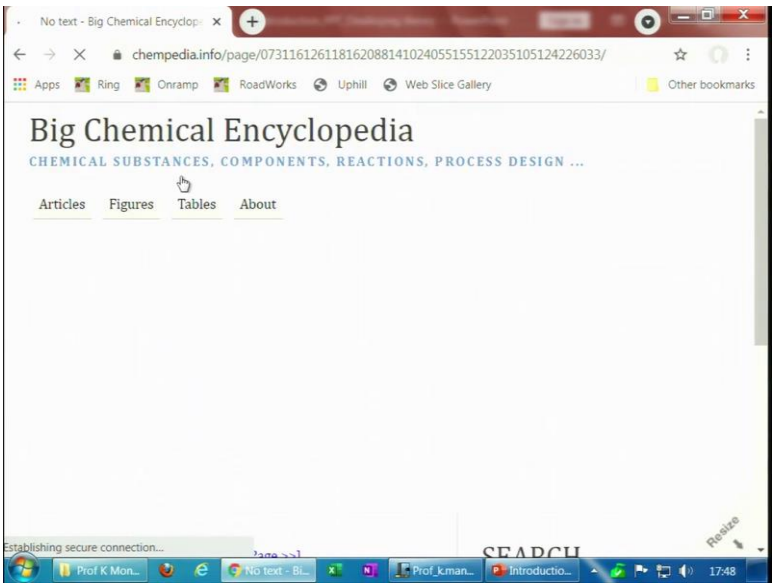

So, that is what this is a plug type ok. So, this is a plug type example and this is taken from National Association of Corrosion Engineers, corrosion this paper by H. M Herro.

So, in that from that paper this picture has been taken, but if you want ready reference, so this particular website you can go and then have a look at it, ok. So, this is entirely for education purpose, teaching purpose fine. Now, coming to the process coming to that particular window where we are looking at the mechanism.

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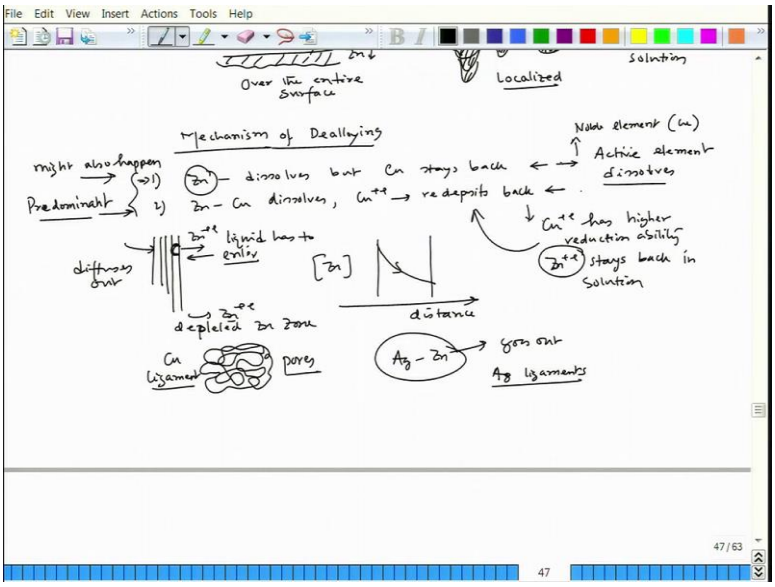

Now, there are different schools of thoughts one is people say that zinc dissolves but copper stays back ok. And another group says that zinc and copper dissolves and then copper ion redeposits back. Now, there are the mostly people believe in that ok and in fact there are other mechanism that when the pores are forming I will come to that pores.

You will see later on I have some pictures, we have done considerable work in dealloying of copper zinc system, zinc copper system as well as silver copper system, I will show some pictures. And there people have also talked about surface diffusion of elements and then accordingly that porous network forms fine.

Now, question is interesting part is both the cases we do not go into the what is the actual mechanism, but if you see interesting part the both the cases the element which is active that dissolves. In this case copper does not go out zinc goes out, but in this case both goes out; both go out first then copper plus plus deposits back.

So, it talks about active and both the cases its active species or active element dissolves fine; active element dissolves. In this case the noble elements the first case noble part,

noble element among copper and zinc which is copper does not dissolve, but in this case both dissolves, but since copper plus plus has higher reduction ability, so, that is what it redeposits back and zinc plus plus stays back in solution.

Now, this dissolution is in the form of ions. So, that is what its electrochemistry that is involved. So, it is an electrochemical dissolution and in the second case its basically electrochemical deposition or we can say cementation fine ok.

So, now, question is people thought that this particular mechanism may not be true because if let us say this is a wall and let us say a zinc goes out. So, there is a small pore is forming or small vacant space is forming. So, that is of the order of one zinc element size atom size.

Now, effect it has to do that way then see this is a small pore the liquid has to also enter. So, this is zinc plus plus and liquid has to enter in order to have an electrochemical contact with the body ok. Then people thought that let us there could be possibility that zinc continuously diffuses out ok. So, this diffusion, why diffusion happens? Because let us say on the first layer or some second layer we have zinc depletion zinc ion is going out. So, there will be depleted zinc zone.

So, now we have a concentration gradient. So, these two layers if I see, so, this is zinc concentration or zinc concentration as a function of distance fine. So, the zinc can diffuse out and then this process will continue. Now, this dezincification happens very quickly ok. We have some data copper zinc if we see, it happens very quickly, but at room temperature even.

Now, at room temperature in order to maintain that supply of zinc for the dissolution to happen that diffusion process cannot meet that particular migration speed, the way dezincification happen over different layers ok.

So, that migration rate is very slow compared to the dezincification rate. So, that gives a suspect that first mechanism may not be true ok, at the same time there will be a small capillary that is forming that pressure capillary pressure that it forms the liquid may not enter ok.

So, there would be difficulty in having those liquids entering into the body for electric chemical contacts fine. So, those are the two regions where reasons that this first mechanism may not be true, but that is what second mechanism has been thought that it is working ok. Now, it is not it is a basically a macroscopically this is fine, but microscopically if we go we will see that when this dezincification happens there is a pore formation ok.

So, these pores forms, these pores are formed because of the dezincification and those ligaments are nothing but the copper ligament fine. Similar situation can happen in case of silvered zinc Ag zinc system ok. So, there also zinc goes out and Ag pore is forming, Ag ligaments are forming ok. So, now, let us see one such picture ok. So, if we remove that.

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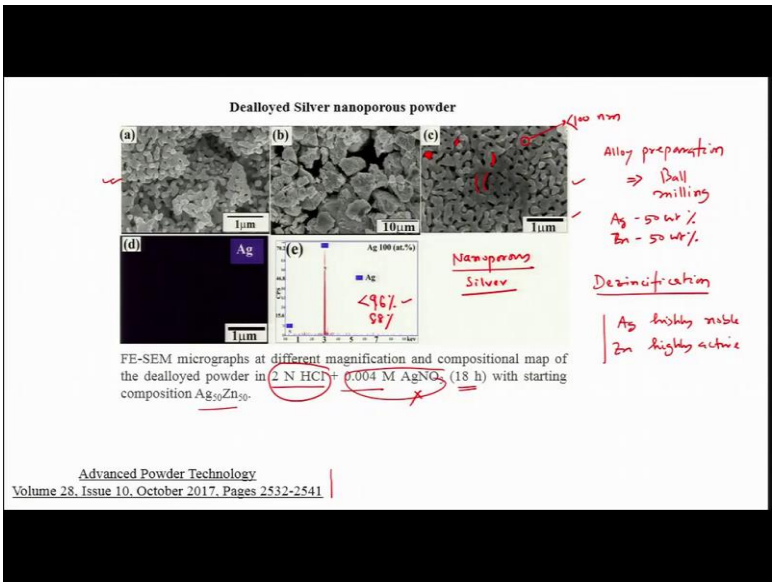

So, let us go to this PPT this is one particular example I would like to show you, this is a paper from this is a, this particular paper if you look at you will see these pictures. This is the work of our group. What we have done? We have this silver zinc alloy we have prepared ok and those we have prepared via ball milling. So, alloy preparation is ball milling. So, it is we have mixed silver and zinc and here it is 50-50.

So; that means, it is a 50 weight percent, this is Ag 50 weight percent and silver zinc 50 weight percent. Now, after that powder we had taken and put it in two normal HCl this is

highly acidic condition and in the two monomer acid and after maybe, after 18 hours; after 18 hours we had taken it out, we had taken it out those powders we had taken it out.

And then we have see it through SEM micro; SEM by Scanning Electron Microscope ok. And we could see that from 50 percent zinc the entire particle, those particles are submicron size particle ok. So, it is a around not sub micron size it is basically around 10 micron average particle size.

Each particle if we look at we will see that this kind of network is forming; this kind of network is forming. And if you again zoom it, we will see this kind of network and if you see this network. So, these are the black spots are this basically, these are basically pores, these are pores fine.

And if you see the ligament, so, this is basically ligament and this ligament its pure silver ok and interestingly the entire particle has become pure silver, 100 percent silver and that we have confirmed by EDS ok. So, and that EDS in SEM we have a facility called EDS, that eds can tell me what is the composition of that particular region where I am taking the same signal signals.

So, this is 100 percent silver. So, this is typically a porous; nanoporous silver. Why nanoporous? If you see the pore size; if you see the pore size, so, this is a small pore size and that pore size if I see the dimension it will be close to around less than 100 nano meter. So, this will come around less than 100 nano meter ok fine. So, this that means, here also dezincification happen, here also dezincification happen, but here dezincification it is not specific to copper zinc its basically in silver zinc.

So, and in case of silver and zinc, silver is highly noble and zinc highly active and due to that silver stays back zinc dissolves, but this silver actually does not stay back it actually dissolves first and then redeposits back. So, that we have seen the solution we have analyzed after the dezincification the initial time for example, when we dip this powder into this solution which is 0.004 molar $AgNO_3$ also we have added.

But, even if we do not add $AgNO_3$, so, in one experiment we have done that $AgNO_3$ was not added, only it was done in two normal HCl that time that silver content was not 100 percent, it was less than around close to 96 percent, we could get 96 to 98 percent

we got we could get. And the solution in the beginning of dealloying we took the solution we analyzed it and we saw silver ion ok good amount of silver ion.

But as the time progresses we saw the silver content, silver ion content in that solution has decreased and zinc content has gone up. And in fact, actually the silver has redeposits deposited back on the surface and that actually forms this nice network of porous body and those ligaments of silver has formed. So, this is typical example of dezincification ok and similar situation if you look at copper zinc system, same situation would appear that there will be a nanoporous copper formation ok.

So, this is one such example I wanted to show you, that in fact, it is not about silver stays back zinc dissolves only initially both dissolves and then silver redeposits back, but there could be possible that the first 2 layer 1 or 2 layer zinc can preferentially dissolve leaving the silver inside that is also possible. So, I would say if I go back to this particular mechanism, if I go back to this particular mechanism.

So, this would be predominant and this might also happen for the first few moments of dealloying, but later on the second part will be predominant ok. So, let us stop here. We will continue dealloying discussion. I will look at the mechanism part or the science part of it in our next lecture.

Thank you.