Corrosion Failures and Analysis
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Lecture - 17
Dealloying or selective leaching: Applications and protection methods

Welcome back to the course Corrosion Failures and Analysis. Today, we have lecture 17 and we will continue our discussion on dealloying or selective leaching. If you recall in the last lecture, we talked about dezincification and we try to look at mechanism of dezincification and if you see carefully, the dezincification starts with dissolution of both the elements; copper as well as zinc.

And then, since copper has higher reduction potential compared to zinc, copper ion redeposits back. We have also seen the same example in case of silver zinc, where silver as well as zinc dissolve and then, silver deposits back leaving zinc in the form of ions in the solution.

Now, we talked about two schools of thoughts. One school says that both copper as well as zinc only zinc dissolves leaving copper behind or leaving noble metal behind. But later one, it was realized that for that to happen you need have a very high diffusion rate of zinc coming from bulk to the surface, but which is not possible at that room temperature.

So, that is what first few layers could be possible that zinc might dissolve preferentially, but in order to have such quite a deep dealloying from the surface, we need to have both the elements to dissolve leaving only the active elements in the solution and redeposition of the noble elements on the surface of the metal.

And in fact, due to that dealloying, we have enrichment of the noble elements on the surface and also, we create a nano porous or porous structure. And then, we also looked at the correlation between dealloying and porosity creation. In fact, also we looked at the correlation between Pourbaix diagram and dealloy, in case of silver zinc system with the experimental data ok.

And the at the end of the last lecture, if you recall that we talked about that this dealloying mechanism or dealloying process has been utilized in order for making some of the exotic systems for catalytic activity like a nano porous gold ok. So, in case of; in case of one experimental process though the application has not been found out yet, but we could make a nano porous silver particles ok.

So, each particle is nano porous with the porosity level of around close to 100 150 nano meter and each around 10 nano 10 micro meter to around 20 micro meter level particles the entire silver particles are nano porous. So, there is no zinc left in that. In fact, in some of the cases, initial alloy composition was silver 25 percent zinc 75 percent, but at the end because of the novel processing we could get 100 percent silver starting from 25 percent in the base alloy composition.

And also, we said that yes, this is advantages in the modern applications of dealloying. It is not bad all the time, but of course, in case of pipeline brass pipelines, it is not good. There could be; there could be possibility of uniform dealloying or plug type dealloying and that would lead to a failure of that pipelines or leakage of the pipeline. So, that is not good ok. So, just let me look at this particular dealloying process little more.

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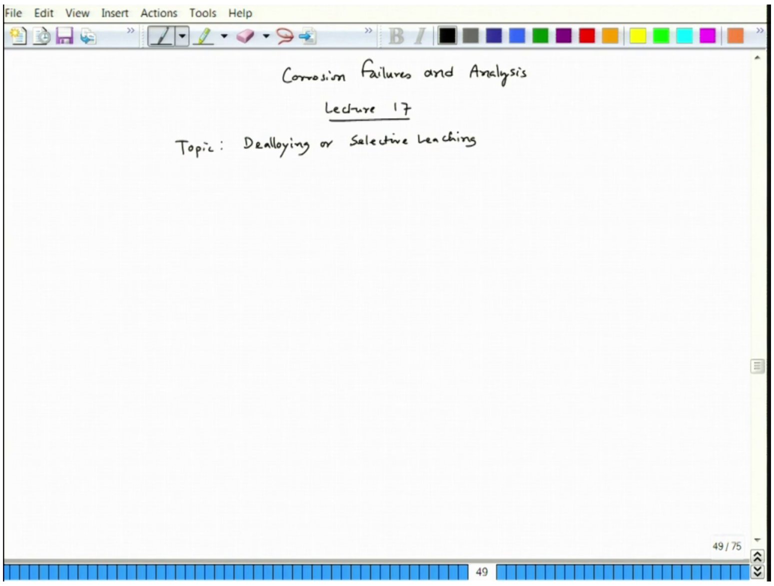

Corrosion Failures and Analysis

Lecture 17

Topic: Dealloying or Selective Leaching

So, this course is Corrosion Failures Analysis. And in this case, today is lecture 17 and topic dealloying or selective leaching. And we will talk about some of the applications of dealloying or maybe, what can be done by through dealloying process.

And also so, the protection processes in case of brass specially, how to stop dealloying, because their dealloying is not good ok. Now, let us get back to some of the pictures. If you see that we started looking at this particular slide.

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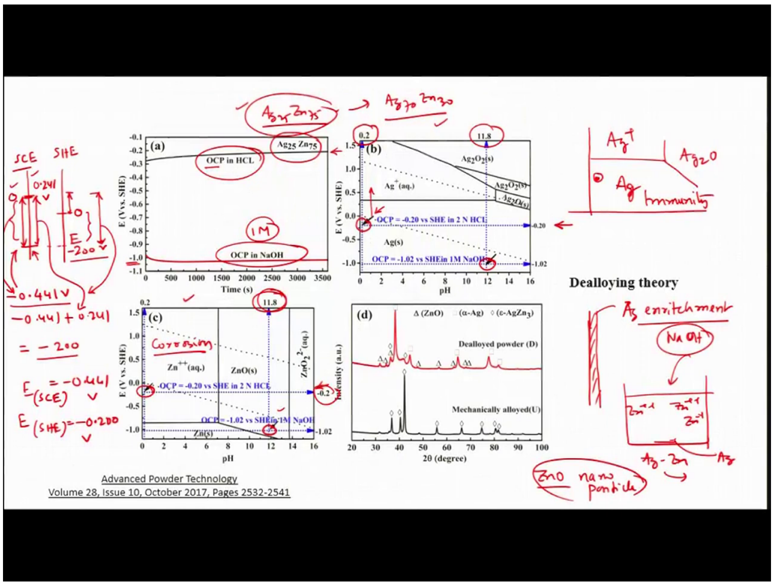

Dealloying theory

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Where we talked about relation between Pourbaix diagram of silver and zinc. And then finally, getting poorer silver. How we get it, because it matches with the pH and potential requirement in the mixed Pourbaix diagram of silver and zinc, where silver should stay as silver, but zinc should dissolve as zinc plus plus.

But once, we change the pH of the solution the potential also changes. As we see in case of NaOH, the OCP changes to a lower value and that time we see that the pH of that higher pH solution and the potential of that alloy, it actually enables us to get a nano particle of zinc oxide ok.

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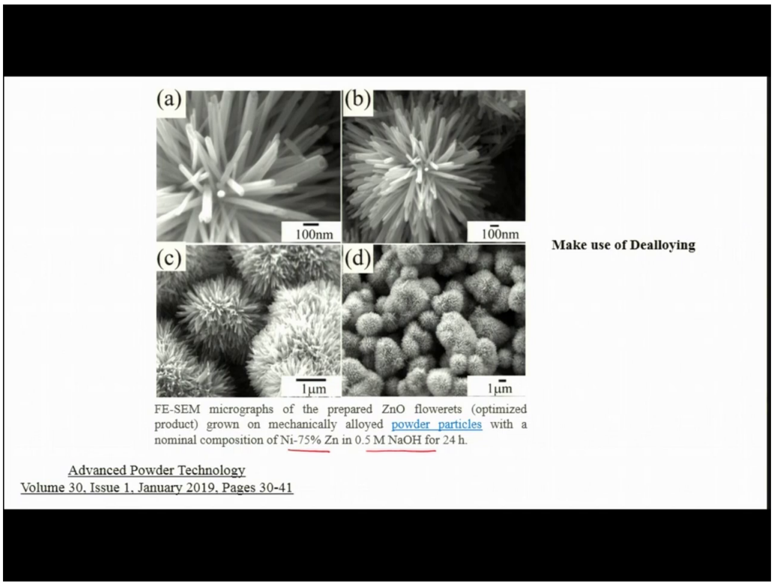

Make use of Dealloying

FE-SEM micrographs of the prepared ZnO flowerets (optimized product) grown on mechanically alloyed powder particles with a nominal composition of Ni-75% Zn in 0.5 M NaOH for 24 h.

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So, now so, the same line what we have seen some of the picture. So, this is one nice picture we have made in the lab scale which is nano rods of zinc oxide while dealloying nickel 75 percent zinc ok. In 0.5 molar NaOH and we get that particular powder. This is the alloy system we made via ball milling and we dipped in 0.5 molar NaOH for 24-hour ok. And while we did that, we got a nice kind of flower kind of structure. So, if you see each particle has become a kind of a flowery structure, which we call it as zinc oxide flowerets ok.

So, this structure we got exactly in the similar process. What we did in case of nickel zinc system also, we made use of this nickel Pourbaix diagram and zinc Pourbaix diagram. And we saw that nickel starts leaving the see zinc starts leaving the surface and in fact, nickel also starts leaving the surface in the form of nickel ions and, but since the pH is in that if you see the zinc oxide zinc pH diagram. So, this particular diagram if you look at. So, let me take that pH just a minute.

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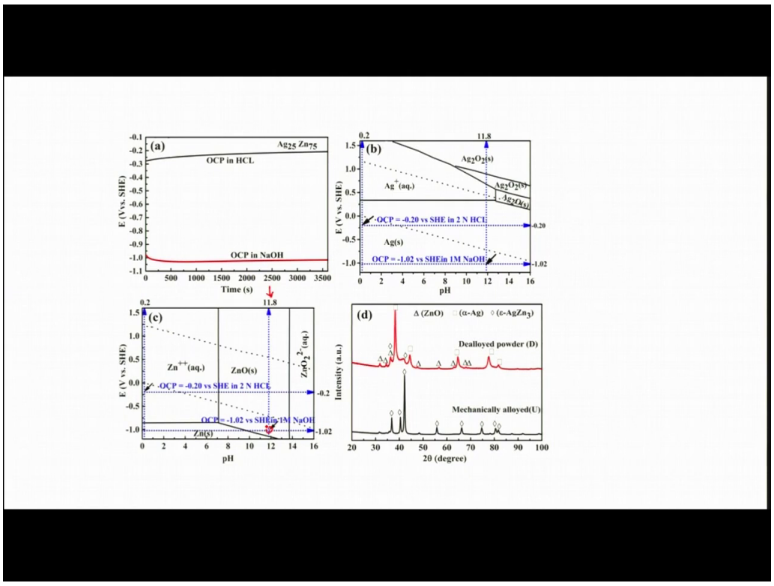

So, I will let me take this particular pH diagram on a separate page. Pourbaix diagram here, what we. If we see this particular position this particular pH and in case of nickel. So, the pH becomes here in this case nickel silver zinc system, but in case of nickel zinc system also, this remains in the zinc oxide level.

So, there in case of nickel zinc system, because of that character of nickel, zinc oxide does not form in the form of nano particles. Rather it forms as in the form of nano rods now, which is hexagonal in nature if you see the cross section ok. So, that zinc nano rod. If you see this particular each one is zinc oxide nano rods and this is hexagonal if you see the top part of it, cross section part of it hexagonal in nature.

And the centre part the core part they are still nickel is left ok. So, it is a basically a on top of nickel zinc core mostly nickel we have created zinc oxide nano rods fine. So, that also tells that both the elements go out into the solution, but in this particular case, because it is 0.5 molar NaOH solution, nickel actually should stay in the nickel form, but because of the interaction of those nickel plus plus and zinc plus plus what is there in the solution.

Nickel does not get the chance to redeposit back rather zinc redeposits back and then, it reacts in that high pH solution with H_2O and forms in an h ZnO and that ZnO actually forms in the form of nano rods. Now, this is again the kind of application of. So, we have utilize the concept of dealloying to make these kind of structures. So, that is what I mean to say that corrosion is not all the time bad.

For example, in case of dry cell; we get the voltage about 1.5 volt, because of galvanic corrosion effect the zinc cell, which corrodes and the cathodic reaction happens on top of the centre graphite or the carbon on the carbon block. So, there we have cathodic reactions and that leads to a voltage of galvanic potential generation. So, that potential is the result of the galvanic affects galvanic corrosion effects.

So, that is the advantage I would say in the reverse in a different manner I would say this is an advantage of, because that situation is persisting, we get that 1.5 volt for making the battery. So, we get electricity out of it. Now, in case of sacrificial protection of steel, we make use of zinc which has much active behaviour in sea water and that zinc actually, corrodes and it protects steel structure ok.

In fact, this zinc in case of sea ship hulls and all those places they put zinc inserts ok. So, that inserts are actually fixed on top of it and that zinc inserts actually give you sacrificial protection. So, this is also an application of galvanic corrosion ok in protection of devices or the protection of components or structures fine. So, this is one such example. Let me tell you we have done further studies and this zinc oxide nano rods can be taken out from the core ok.

If we do a strong ultrasonic vibration those zinc oxide breaks open from the core and then free standing zinc oxide nano rods we could get. And that nano rods we try to see what is its effect in breaking methyl blue, which is a kind of bad things which is actually not environment to a very environmentally very dangerous component, which is available in case of when we have colouring plants.

So, there this methyl blue it can crack those methyl blue and so, that we can get a water which is free of methyl blue. So, that zinc oxide this zinc oxide has shown this property so; that means, starting with a nano dealloying concepts, we could get this nano porous at this nano this zinc oxide flowerets on top of a nickel core.

And then, we could break open this zinc oxide nano rods and those nano rods were utilized in cracking methyl blue ok. So, this kind of application we can think of ok. So, you can actually make use of some bad things into a good thing ok. So, that is the major purpose of discussing this particular issue ok.

So, now, coming to applications this is coming to this dealloying phenomena in others situations for example, if you take steel let us say ok. So, there also you can sense dealloying. If you have heard of some of the structures what we get in steel. Let us say, you take a carbon steel and in that carbon steel if you take 0.7 percent, which is Indian rail steel around point say 7 percent carbon. So, that is that micro structure if you rolled that rolled rail if you take it out and then see the micro structure under SEM, you will see it is a pearlitic micro structures almost 100 percent pearlitic micro structure ok.

Pearlite is a mixture of two phases; one is cementite another one is ferrite ok. So, that structure we get my or call it micro structure we get in pearlitic micro in 0.7 percent carbon steel, which is the typical composition of Indian rail steel the carbon contain of Indian rail steel. Indian rail steel is basically carbon manganese steel ok.

So, now that steel you can make out those structure, because of basically galvanic effect the galvanic effect also leads to dealloying ok. So, I will see that example. Even there could be another structure that you one can make that structure is called spheroidal cementite structure or spheroidal steel. So, the spheroidal steel is those cementite lamellae pearlite that can be converted into small small spheroids ok.

So, those spheroids will be sitting in the ferrite matrix ok. So, that structure has got a very high ductility fine. So, in if you compare the pearlitic micro structure steel and spheroidal micro structure steel. The spheroidal micro structure steel will have a higher ductility. So, in those cases, we do experience this dealloying effect ok.

In fact, the dealloying though its is basically a specific it is basically removal of one element out of the entire alloy systems. In case of; in case of pearlitic as well as spheroidal steel, we also see that it is basically a selective dissolution of iron leaving cementite behind ok. So, that also can fall under the regime of dealloying ok. So, let us see some of the examples.

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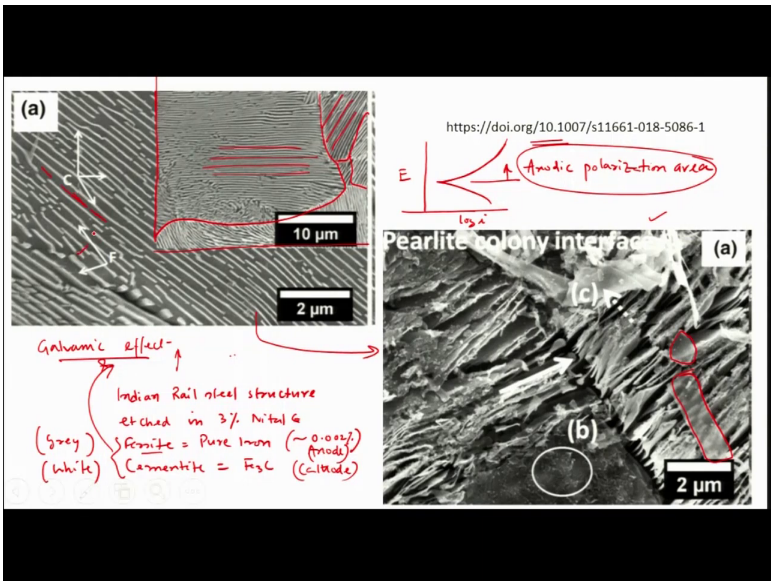

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Galvanic effect

Indian Rail steel structure etched in 3% Nital

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

(white) Cementite = Fe_3C (Cathode)

Anodic polarization area

Like if you see this structure this is basically the left structure. So, this structure if you look at. This is typical Indian rail steel structure fine. So, which is almost fully pearlitic. This is etched in 3 percent Nital ok after doing all the micro graphic steps and this is the book this is the paper you can refer this is the work of our group at IIT, Kanpur.

So, now, these structures. So, these white things, those are carbides. So, it is written here these whites white lamellaes form pearlite has a typical lamellar form, those are carbides and this grey part is basically ferrite ok. And ferrite is nothing, but almost pure iron. Since, the carbon content is of the order of which is maximum carbon content 0.002 percent.

So, that much of carbon is there in ferrite at room temperature ok. So, that is a very very minor carbon content. So, you can say that it is almost pure iron. So, now, and also if you see this is actually low mach picture. So, the inside part this is the part this is the low mach picture. This is also SEM picture and if you see some kind of boundary, this is the boundary. So, these are actually nothing, but pre-austenitic gain boundary. Because while making this it was the steel was taken to more than 900 around 900 degree Celsius more than little more than 900 degree Celsius and then, air cooled ok.

So, that time that austenite that forms at a around 900 degree Celsius I think around 800 to 850 around 850 to 900 degree Celsius. So, the austenite grain forms there and when you cool it down, the pearlitic nucleation starts at the grain boundary of pre-austenitic grain boundaries ok. So, that in along the grain boundary.

And that is what if you see each grains, the pearlite orientation so, are actually similar. So, for example, here the orientation is like this here the orientation is like this. So, each grain you will find one set of orientations ok. So, that is what also those are actually a kind of it gives an indication that those are kind of pre-austenitic grains ok previously before pearlitic nucleation.

Now, this structure is forming, because of etching and what happens during etching. During etching, ferrite if you compare the cementite which is this is carbide or cementite here, the cementite white portion this is grey portion grey portion and white portion cementite which is Fe_3C.

Now, here ferrite and cementite; if you compare their potential or potential developing in 3.5 percent initial solution. So, this is done in 3 point this is done in Nital, which is nitric acid solution ok. So, there ferrite acts as anode and cementite acts as cathode. So, of course, there would be galvanic of effect and ferrite starts dissolving ok along the along the lamellae portion.

So, this particular portion basically, those are the dissolved part little bit of dissolution happens and that is what you are developing a protrusion around that cementite portion and that is what you could visualize or visualize those cementite and say ferrite, because of the; these are the typical such kind of phenomenon galvanic effect rather. Now, after that this particular steel without etching. See, this is etched structure and if you do not etch, you do not see those kind of structures.

It is a absolutely it will be a smooth structure. You will not find any sort of features the way it has been developed here. Now, if you take that sample and you polarize ok. So, polarization is basically you are taking the potential E and this is log i; that potential you are taking from low potential to high potential ok. So, this is the polarization simple dynamic polarization you are doing.

And after dynamic polarization, we saw typical this kind of structure and interestingly here you see that some of the plate kind of structures you could see ok. So, these plates are nothing, but cementite ok. So, those cementites are actually plate nature having a plate nature and that, because of excessive dissolution of ferrite which is happening around this particular area, which is basically called anodic polarization area.

So, there you have excessive dissolution of ferrite, which is happening forcefully ok, because we are forcefully taking the ferrite out. Here, we are not doing forcefully, because this etching is done at a normal corrosion potential, which is rather we call it open circuit potential, but here we are taking those ferrite out forcefully, because there this particular action is taking place ferrite is acting as a anode and cementite it is acting as a cathode. And cementite does not dissolve, but ferrite dissolves leaving those plates as a free stand it past standing particles ok.

So, that is what these plates are coming out on top of it. And now, actually this particular steel has been made into this same steel same composition same micro structure, but now since, because of this electro chemical polarization to a high anodic potential, we have taken the ferrite out it is a basically leaching the ferrite out, which is nothing, but the pure iron and then leaving cementite back behind ok.

So, this is a typical case of dealloying you can say which, where iron comes out leaving the and cathode part behind, but here interestingly; it is not about both the things are depositing dissolving back and one is depositing back. Its basically, the anodic component dissolve preferentially leaving the cathodic component back. So, this is happening, because we are doing a forceful anodic polarization forceful taking out of ferrite part or pure iron part. So, here, iron dissolution is taking place preferentially; that is got that is why we can put it under dealloying effect ok.

So, this is dealloying effect. It is basically a result of galvanic corrosion. So, this is as a result of this dealloying what we are getting is a result of galvanic effect. So, now, another example let us look at.

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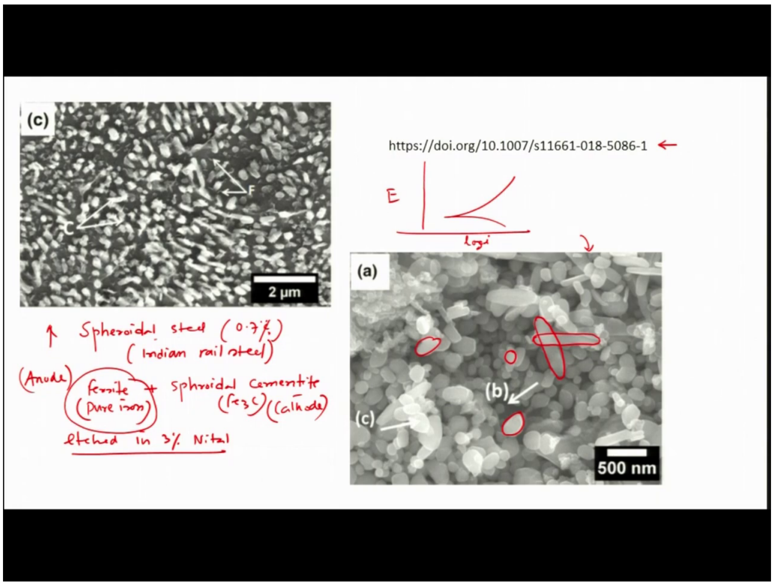

https://doi.org/10.1007/s11661-018-5086-1 ←

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

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

etched in 3% Nital

So, this is one of another structure, which is spheroidal steel and here also, the carbon content was. 3 percent carbon, which is weight percent. And this is actually Indian rail steel and if you want to know how it has been made, you can look into this particular paper which is our work ok.

So, to work at IIT, Kanpur. Now, this where what we have done. If you see this particular structure and this particular structure. So, this was the structure in the begin which is the fully pearlitic structure. And then, we have broken those pearlites or cementites ok cementite lamellaes we have broken by doing heat treatment and then, we have made small small spheres or near spherical or a kind of electrical ellipsoid rather those cementite particles have formed in the ferrite matrix.

Again, it is the mixture of ferrite plus I can say spheroidal cementite, which is Fe_3C and this is pure iron right. Now, similar way this is actually etched structure etched in 3 percent Nital ok. So, this is in Nital etch solution. There also dissolution of ferrite happens, but not to a aggressive extent. Only, the surface dissolution take place and that is what you have these features and if you do not do in etching. If you see under microscope, you do not see anything.

Now, once we do dealloying in the by the way of polarization again, we do such kind of polarization and after polarization, we saw this structure. And remember after polarization in the previous example, where we talk about 100 percent pearlite. There also we have not done any etching. So, that polarization actually laid to that structure. Here also, there was no etching after polarization. It is a basically on each sample polarized and then, we should look it under microscope SEM.

And here, you could see, that to cementite particles can be clearly visible. So, the each one is a cementite particle. And if you would see that those cementite particles are actually hanging if you see those hanging cementite particle there is some cementite particles it.

Since, it has started from a lamellar cementite, some of the cases it could not break open. So, you could see a long cementite. A part of the lamellae is still existing, but many of them have to actually turn into a small small spheroids or ellipsoids ok. So, those are actually structures. This is again happening, because its a preferential dissolution of pure iron ok. Pure iron dissolves and leaving behind cementite. This is also a galvanic effect. Since, ferrite act as anode and cementite act as cathode and preferential dissolution of anode happens leaving behind those spheroids of cementite ok.

This is also typical example of you can say the typical example a dealloying of pure iron leaving cementite behind ok. So, in that aspect you can say the first logic, where it says that pure element goes out active element goes out and that noble element stays back. Here, cementite is not an element. Its a kind of compound, but still, we say that noble element preferentially goes out. Exact similar situation happens in case of cast iron ok.

So, cast iron is nothing, but iron carbon alloy system, where carbon stays in the form of graphite not in the form of cementite ok. So, during that period also graphite is also highly cathodic to ferrite ok. So, when it happens; ferrite dissolves leaving behind graphites. And if you take a spheroidal graphite iron, which is called S G iron. If you put it in acid, you will see after sometime at the bottom of that particular container, you will see black dark black graphite particles are there.

Because in case of spheroidal graphite iron, we have cementite this graphite in the form of spheroids. So, once those dissolves, those graphites falls off ok. So, that falling off of graphite leads to the graphite deposits at the bottom, but if it in case of grey cast iron, where the graphite forms in the form of needles ok.

Those cases and it is a basically those cases graphite is not able to fall off rather it stays back, because there is the interconnection or mechanical locking of those graphite flex. So, that is what the graphite flex stays back.

And you will see the color changes to a greyish mode and if you mark with that particular graphite on a white paper, you will see that the way marking happens when you use pencil, similar marking happens when you use grey cast iron. We will talk about that grey cast iron part in our next lecture.

So, till then you could see that other system in steel also, we can experience dealloying ok, but in case of graphite in case of grey cast iron or SG iron we will see how it forms the way I have just explained little bit. So, we will take this expansion in the next lecture.

Thank you.