Lecture - 07
Explanation of Corrosion Processes on the basis of Mixed Potential Theory: Part I

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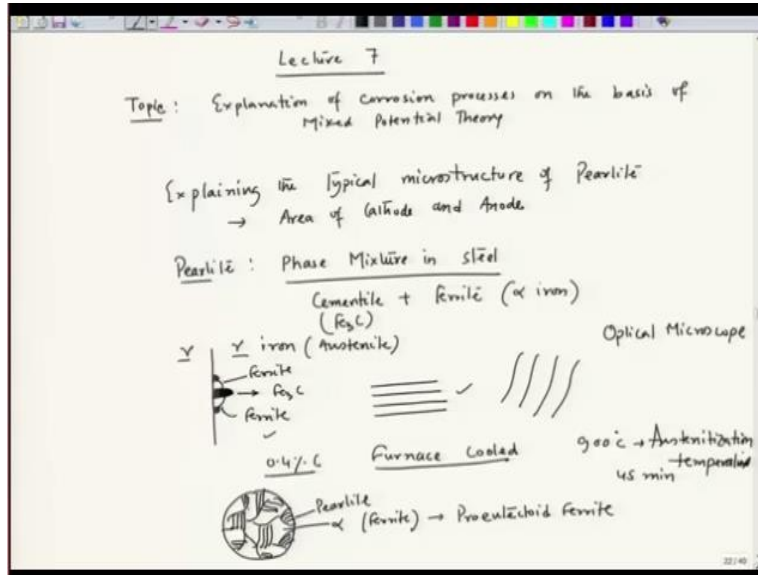
Hello everyone, let's start lecture 7 and topic we will now continue our discussion on explanation corrosion processes on the basis of mixed potential theory. Fine. We in the last lecture at the end we started talking on the evolution of micro structure of pearlite and how it looks another microscope, optical microscope this has relation to the area ratio of a galvanic couple.

So, let's explain that particular micro structure, so it is actually a practical aspect of corrosion. So, how to or explaining the typical micro structure of pearlite, so this is related to area of cathode and anode. Now in steel the pearlite is a phase mixture in a steel and that to we get it very low carbon steel let's say 0.1% carbon we do not see the pearlite much.

But as we increase the carbon content let's say if you go to 0.4 to 0.5% carbon we can clearly notice pearlite. And in the pearlite the phase mixture, why call it phase mixture because it consist of 2 phases one is cementite and another one is ferrite. So, ferrite is nothing but alpha iron which is a solid solution of carbon in BBC iron and cementite Fe_3C this is a compound. Okay.

Now their formation happens due to nucleation and growth phenomenon, so either ferrite or cementite nucleates on a grain boundary and that to in the pre austenitic grain boundary and then gradually by the side of it. If cementite nucleates by the side of it ferrite nucleates and then gradually this nucleation happens at the same time side by nucleation keeps on happening at the same time you have the growth of this ferrite as well as cementite into the austenite grain.

So, that means if we have a austenite grain boundary like this, so then if cementite nucleates, this is a cementite let's say or I would say that Fe3C. Fine. And then since cementite takes carbon from the austenite, this is austenite, austenite it termed as gamma iron or austenite. So, since carbon diffuses and then forms Fe3C and the carbon in the Fe3C is 6.67 in terms of weight percent, so the surrounding area would be depleted in carbon.

And this particular steel from the austenite it has been taken to a region below eutectoid point. So, that time by the side you will have a ferrite formation, this is ferrite. So, now by the side then there will be a cementite nucleation again, cementite formation, so like that where at the same time they keep growing along this direction. Fine. So, finally your structure would be, so this is cementite, this is another cementite, this is another cementite.

So, like this it forms a lamellar structure and this lamellar, so their growth may not be absolutely a kind of a flat parallel lines, they are actual look like this. Okay. So, that time this is the look what we are getting in under the optical microscope. Now if we take of steel where let's say 0.4% carbon steel and that is annealed furnace annealed. So, that means I would say not furnace I mean I would say furnace is cooled.

So, that means you take it to 900 degree Celsius, this particular carbon steel then wait for sometime let's say half an hour. So that the complete austenite forms in that particular micro structure and then you allow it to cool in the furnace by putting off the furnace. So, that time you will have a slow cooling and once the temperature crosses below eutectic temperature which is around 727 degree Celsius and then you will have this politic reaction, this kind of structure evolves.

So, then you do this is the austenitization temperature for half an hour or let's say 45 minutes just to be on the safer side. So, that every carbon goes into the solid solution of gamma iron and then you cool it slowly furnace cooling. So, you will have a structure like this, so you have austenite ferrite grain and then you have pearlite. So, like this a kind of structure you will get, so where these are the pearlite and these are alpha iron, alpha phase which is ferrite.

So, these are the ferrite which has a special name called proeutectoid ferrite. So our interest is not on the detail of phase transformation. Our interest is why it looks like this there is a black strips in the bright background.

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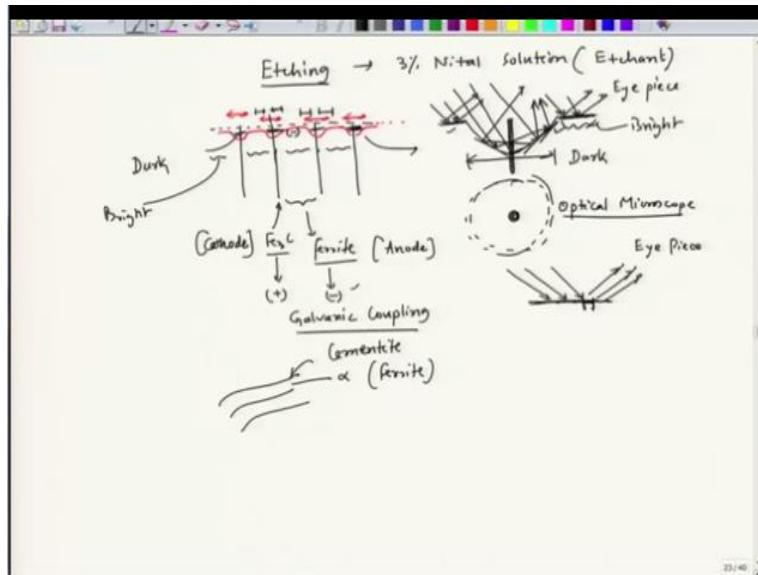
Now in order to understand this we need to understand little bit of etching and this kind of steel is etched in around 3% nital solution and nital is a mixture of nitric acid in alcohol. So, these nital solution you first have the sample you polish it go up to the mirror polish. So, that you can see your face are reflected on that polish surface and then you hold it with a tweezers take this nital solution on a petri dish and then dip that particular surface into the acid wait for maybe 2, 3 seconds or maybe maximum 4, 5 seconds.

Depending on how much change you are facing you are experiencing on the surface it will turn into little grey little a darkish appearance that means the surface is getting attack by that particular solution and that particular process we call it etching. And this is nothing but etchant, we call it

etchant. So, now that chemical reaction, we call it chemical reaction but actually it is not chemical reaction, it is electro chemical reaction.

And because of that particular electrochemical nature of that reaction, we get to see appearance like this under optical microscope. So, now what exactly happens, so now you have those lamellar is not it. So, you have ferrite, you have cementite like this, those are aligned like this in a particular pearlite colony. So, these are cementite and this white portions are nothing but ferrite. Okay.

So, now when this surface is attacked typically if we compare this 2 phases their electrochemical behavior this has higher potential in that galvanic series as compare to the ferrite. So, these acts as a positive terminal and these acts as a negative terminal in that galvanic couple condition, so, they are actually forming a galvanic coupling. Fine. So, once they form galvanic coupling since this is negative that means this is anode and this becomes positive that means this is cathode.

So, cathode would not dissolve, anode would start dissolving but interesting part is if we see this particular surface this part is negative, this part is positive. So, dissolution would follow the pattern what we have experience before.

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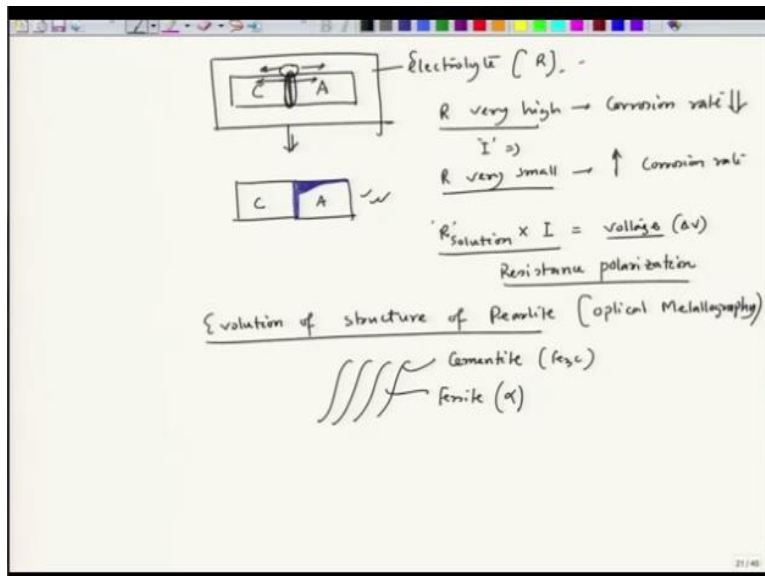
So, the experience we have experience like this that in the dissolution would be more pronounce near to the galvanic couples region. So, now if I consider here also the dissolution of ferrite will

be more pronounce around this region. Similarly, here the dissolution would be more pronounce around this region. Fine. Away from that the dissolution of course it will dissolve. But the dissolution rate would be slower because of the resistance offered by the electrolyte away from the galvanic coupling or the point where the other line where the galvanic coupling has been set up.

So, now if they dissolve like this if we put it in a red colour, so now their dissolution pattern would be like this. Fine. So, that means you see that this is the surface line, so everywhere that dissolution has taken place but the dissolution is more pronounce around this segment. Now if you see if you zoom 1 particular region this is the cementite. Okay.

Now here we have situation like this. Okay. Or depth. Now how do we see the structure in optical microscope. We see it because the light which is falling, so you have a surface the lights are falling and then they are getting reflected and you have an eye piece. So, this eye piece you look at and then see the structure, so basically it is a magic of reflection of light in the optical microscope. Okay.

So, now when you have a situation, if it is a flat surface before etching it is a flat surface and it shines why it shines because all the points over which those reflections are taking place of the light are happening at the same condition. And the energy of the light which is coming out or almost of the similar range, so that is what there is no multiple reflection within a small region.

If we consider this small region not much of multiple reflections are taking place within that particular zone, so that is what we are having appearance of a very shiny surface. But if I consider a situation like this, so the here the lights are falling, here also lights are falling, so they are reflected. And since it's a almost kind of a flat region a near flat region, so the surface look this surfaces from this particular zones.

This surfaces are this section or this section they look shiny or the bright but if I consider here in this zone what happens. Let's say 1 light has fallen like this, now here we have to consider are reflection angle, now it will go like this. Fine. And when it goes like this that could be hindered

by this cementite plate thickness or if that reflection because if we consider the cross section, the cross section looks as a circular region. On the center we have cementite.

So, if it is falling away from that particular if it reflecting away from that particular cementite rod, rod like a plate like appearance. So, then it will have a reflection here multiple reflection and then again you will have a angle like this, it will go like this. Okay. So, it is not coming back to the eye piece here we have eye piece. Fine. Similarly, if another light falls like this, so you have angle like this it might go like this. Fine.

So, like that there could be a multiple kind of reflection that will take place, so those reflections might not come back to the eyepiece. So, if they do not come back to the eye piece, so that means the energy that is being taken by those rays, I would say that the number of rays coming out from those regions, this particular region will be less than the lights coming out from this flat region. So what could happen? It would look like a dark region.

So, if something looking dark within that it is small a pin kind of thing or the plate kind of thing that would look like a dark object. Okay. So, that is why we see this particular cementite to be dark and interestingly this darkness comes because of multiple reflection and those lights will not come out to the and it will not go to the eye piece. So, it will look dark and this region will look bright, so this region will look dark and this region will look bright.

So, if we consider here this section, so this section, they will dark they will be dark and this region will be bright. So, the and interestingly these are the regions of the dimension is pearlite of few microns maybe around 10 to 20 microns. So, that time, so if this is that much dimension, so then what happens. In the optical microscope the resolution is less, so it will not be able to gauge the position of that cementite properly only it will show a kind of dark patch around that.

So, that for the Final micro structure would like this where this is alpha or ferrite and this is cementite. Fine. So, this so why we have explained this because it has a relation with the area and the resistance affect during electrochemical etching process. And these relates to the understanding what do we had in our previous lecture is this.
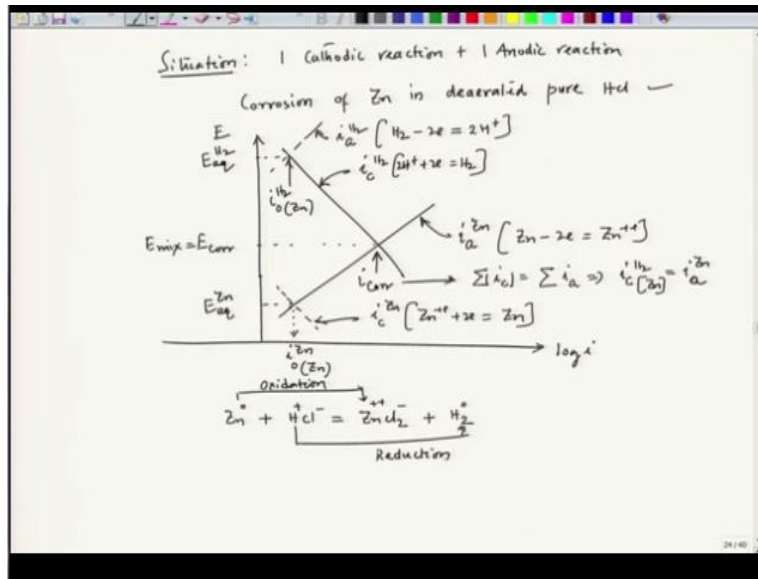
So, let's go to understanding of those 5 instances, the situation, 5 situations what we have talked about. Now first instance is situation or instance or situation is here we have 1 cathodic reaction + 1 anodic reaction. So, in this case we have already explained this before while we consider corrosion of zinc in deaerated pure HCl. So, that case our mixed potential theory was, so this is E, this is log i and the plot look like this.
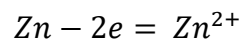
So, this is i zero for the zinc over zinc surface, this is i zero of hydrogen over zinc surface, this is ia of hydrogen, so that means
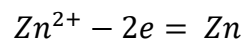
$$H_2 - 2e = 2H^+$$
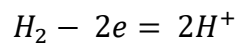
this reaction would happen. And this line corresponds to ic

$$2H^+ - 2e = H_2$$
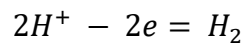
this line corresponds to ia zinc which is nothing but

$$Zn - 2e = Zn^{2+}$$

and this line is ic zinc which is

$$Zn^{2+} - 2e = Zn$$

and this is the point which is E mix which is nothing but E corr and this point is i corr.

And this current density meets the basic of mixed potential theory where it is ic = ia is nothing but ic hydrogen over zinc surface equal to ic zinc ia zinc. So, that means this is the complete picture of that particular mixed potential theory for explaining this particular situation. We have already

explained it in detail I think end of fifth lecture. So, the overall reaction is overall electrochemical reaction is

$$Zn + 2HCl = ZnCl_2 + H_2$$
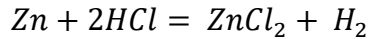
where this is + this is zero, this is + +, this is -, this is -, this is zero. So we have oxidation, we have reduction. Fine.

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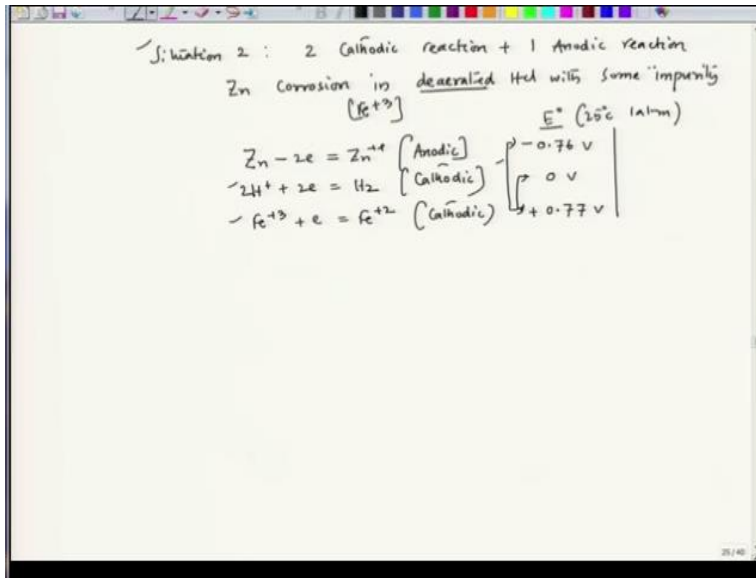
So, let's go to the situation where we have considered 2 cathodic reaction and 1 anodic reaction. Now this particular thing can be explained can be observed when which is zinc corrosion in deaerated HCl with some impurity in the form of Fe+ 3 ion. Now a deaerated means that HCl does not have any dissolve oxygen. And that particular so interestingly, so if you leave HCl in the atmosphere it will always have some dissolve oxygen.

Now how do we take care of that oxygen, how do we take out those oxygen dissolve oxygen from the HCl. So, what in the lab scale what is done is we purge nitrogen into the solution. So, the nitrogen bubbling happens and that releases dissolve oxygen out of the HCl solution. So, this impurity Fe+ 3 is a small impurity very small amount some ppm level. Okay. What would happen?

Now in this case let's first analyze what are those 2 cathodic reaction and anodic reaction. So, the anodic reaction it easy to understand it is Zn - 2e = Zn^{2+}. This is anodic 1 anodic. Now one of the cathodic reactions of course if it is an acid solution, so the cathodic reaction of course this is the cathodic reaction and we would we do see that hydrogen bubbling is taking place on the zinc. Now

interestingly just before going into this explanation the observation that has been observation is typical observation is.

If you consider this particular case, here also hydrogen bubbling takes place on the zinc surface and here also hydrogen bubbling takes place on the zinc surface and we do get zinc corrosion. Now the hydrogen bubbling at amount I would say that the bubble form across the surface would be much less in this case as compare to this case. So, we would also understand that particular observation through mixed potential theory.

Now this is cathodic reaction, now where is the another cathodic reaction. The another cathodic reaction happens in this form. So, this is also cathodic reaction and interestingly this is a very very strong cathodic reaction why, so if we consider standard reduction potential E zero. This one is -0.76 volt, this one is zero volt and this one is+ 0.77 volt ok and that to all at 25 degree Celsius and 1 atmosphere pressure. Okay, so that condition these are the potential the standard reduction potential.

So, now we can see that the difference between this 2 is huge, so that means and also even if we consider these 2 the difference is huge. So, that means this is a much stronger cathodic reaction than this, so now you could see that there are 2 cathodic reactions and 1 anodic reaction. And overall process of course zinc would dissolve and these 2 cathodic reactions would happen on the surface of the zinc. So, we would analyze this particular situation in our next lecture, so let's stop here, thank you.