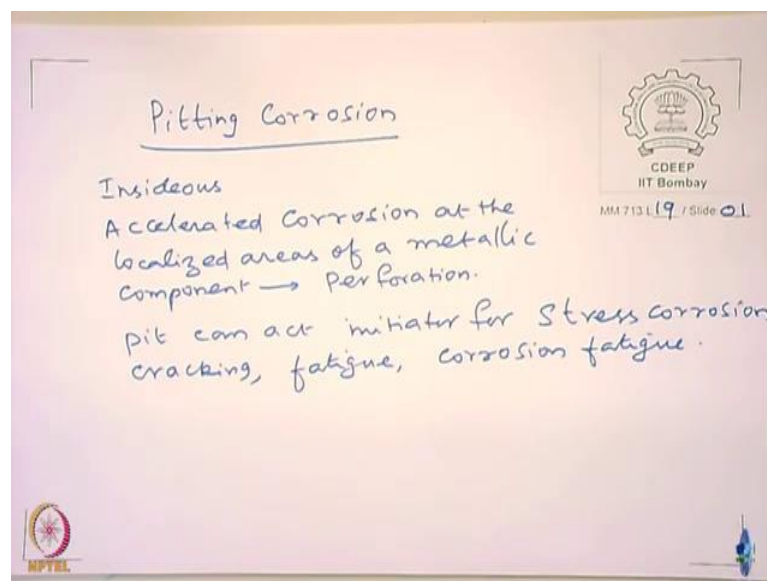


Aqueous Corrosion and its Control
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Lecture – 19
Forms of corrosion: Pitting corrosion (Part-1)

Today, we shall discuss an important topic which is Pitting corrosion. Pitting corrosion of metals can cause a severe damage to the structural integrity.

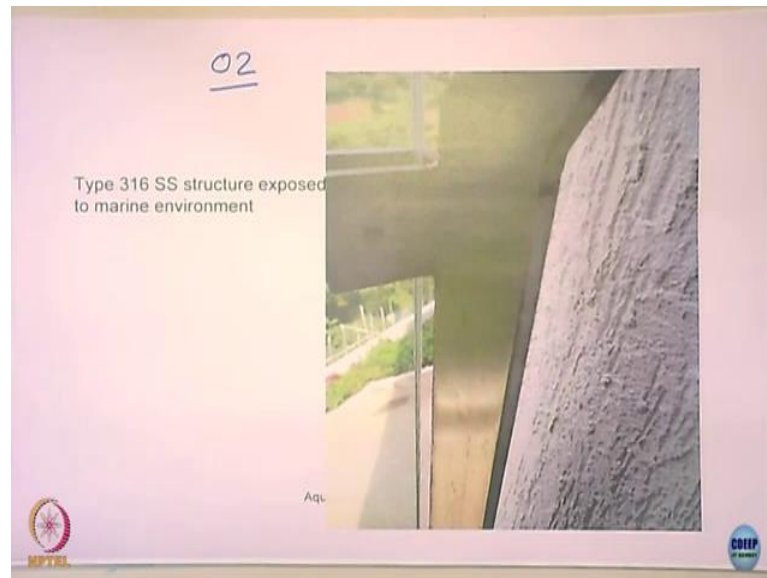
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Because the rate of corrosion in the pit can be very high, it can be about a million times higher corrosion rates as compared to the surrounding matrix. So, the pitting corrosion is very insidious. It can cause accelerated corrosion at the localized areas of a metallic component. It can ultimately, can lead to perforation, it can be a leak. Sometimes the pit can act as initiator for say stress corrosion cracking. It can be initiated for simple fatigue or it can be even corrosion fatigue.

You know the reason because when you have a pit which is very localized, it can be a stress riser, the stress intensity at that location can be quite high and so, the crack can initiate and grow even below the yield point of a metal. So, pit is in fact, is very detrimental it can bring down the component life quite significantly, leading to premature failures.

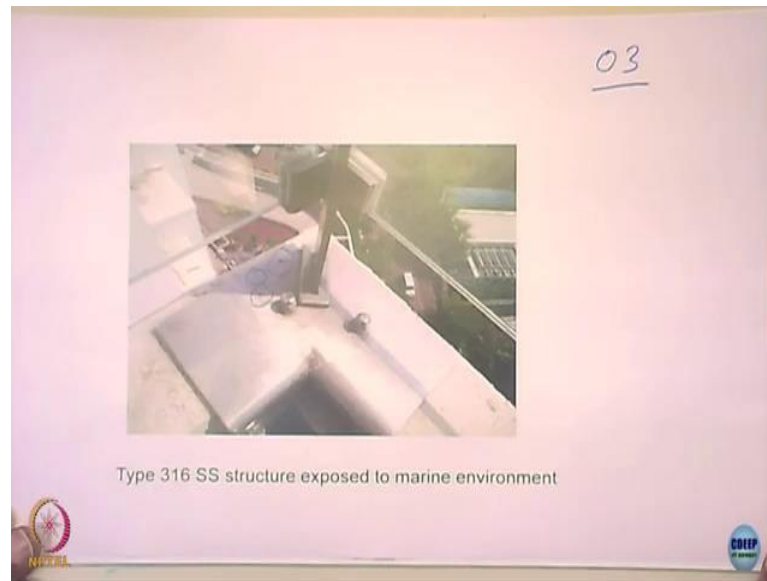
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Now, I will just want to show some illustrations, how this pit can be look like. I do not know how clear it is to you, it is a long shot and taken on facade. This is stainless steel; this is you can see there is a stainless steel here right. You can see here it is a stainless steel and you see some fine dots appearing right. And these fine dots are actually pits and these pits are appeared within about 6 months to 1 year of commissioning of this particular structure.

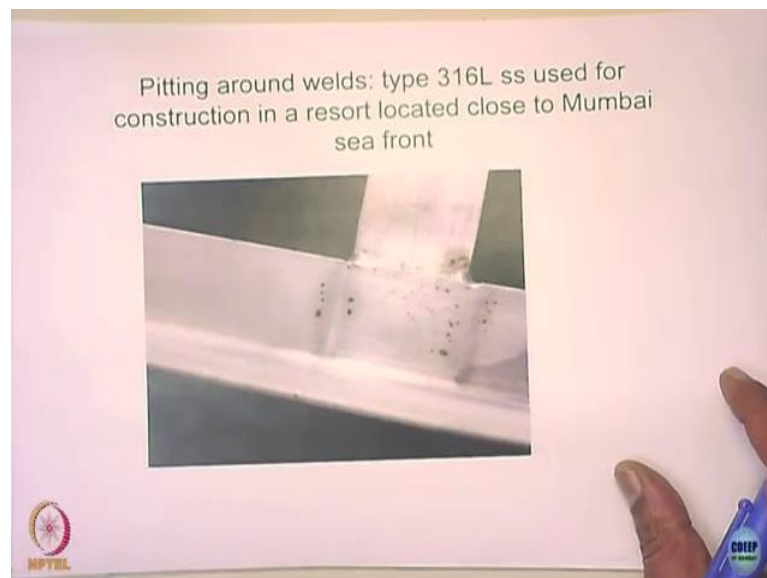
Because it was at the seafront and the seafront you know that you have lot of chlorides being carried by the wind and the chlorides deposit on this stainless steel structure that leads to pitting corrosion. And this civil engineering structure, you know it is you would in the same location.

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You will see here, slightly better I suppose. You can able to see a pit here right, you can able to see a pit around here and a pit around here and you see pits here right. So, and of course, this has tiny pits somewhere around here, you can see lots of tiny pits which are visible to the naked eye and again, it is a 316 stainless steel. You could see the pitting happening within 6 months to 1 year ok. They become very severe, where they were welded. See that here right, right. I hope you were able to see this.

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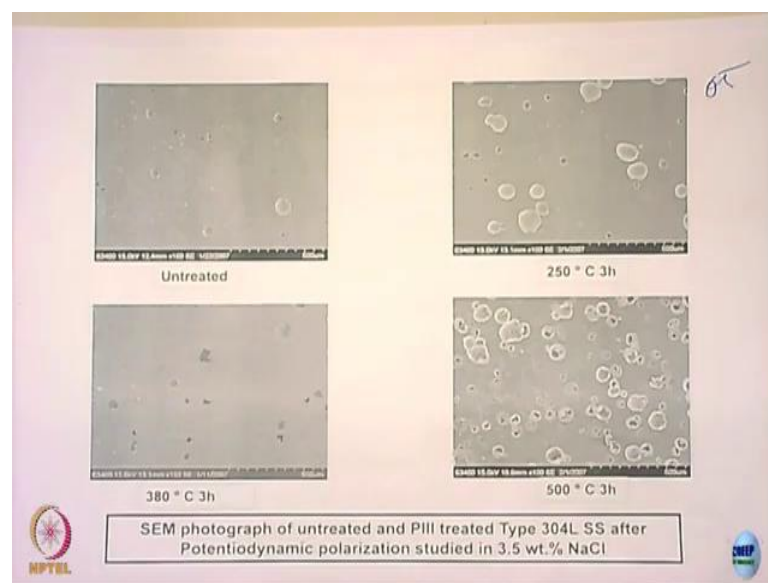


Student: Yes.

Reddish brown spots ok; these spots, they do correspond to severe pitting. Two kinds of problems here; one is the loss in the structural integrity, otherwise the cosmetic appearance of this stainless steels right, you have a reddish brown color and especially, you are talking about household appliances or the facades of a house and which are all can cause you know a kind of appearances which are not really acceptable.

Now, these are all macroscopic view on the pits and if you see in the microscope sometimes, these pits appear to start with the microscopic levels actually.

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You guys are all know right, you earlier have seen that what is polarization and how the polarization of passivating metals look like, when you anodically polarize you get a passive region and you rise a potentially further, you get into pitting regions.

And if you look at the samples after the anodic polarization and you will see a very microscopic pits here ok. You see these pits all are very microscopic natures, many of them are all hemispherical in natures that is how the pit starts actually ok.

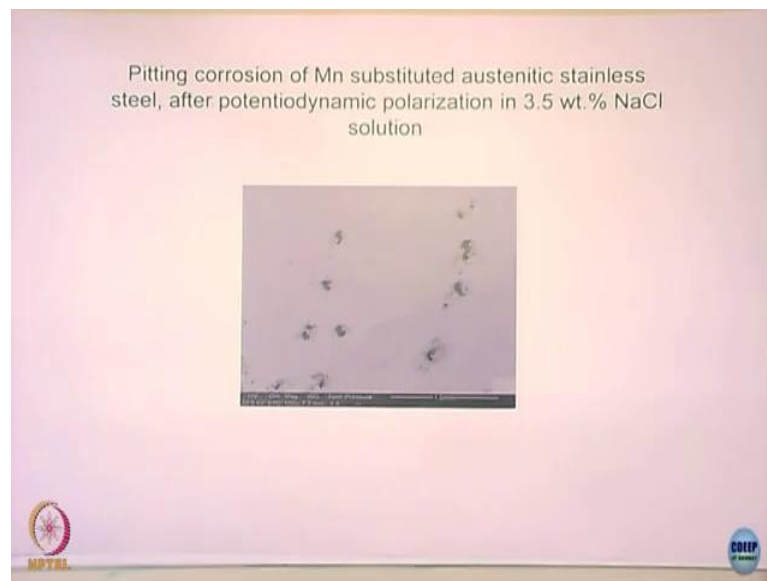
In fact, the pit could start at the submicroscopic level actually; you know submicroscopic means less than 1 micron actually, can happen. So, these are the kind of pits happened in the case of a stainless steel which is 304L stainless steels and this stainless steel you know plasma ion implantation technique ok, where you implanted nitrogen in the stainless steel and you can see here that it is untreated right and treated with the nitrogen

and you can see that the number of the depth of pit here is reduced as compared to over here.

So, in this case nitrogen addition is improved. Of course, the treatment was done at different temperatures. At a higher temperature, you can see that the pits become more. Essentially, this is a PhD work ok; wherein, they converted the surface so that it can have higher pitting resistance and higher passivation.

In that case, they have added nitrogen by plasma source ion implantation or also called as plasma ion, plasma immerse in ion implantation technique. So, essentially, I want to show that these are all can be microscopic, you can start with it can be even sub microscopic levels, these pits start and then, they grow.

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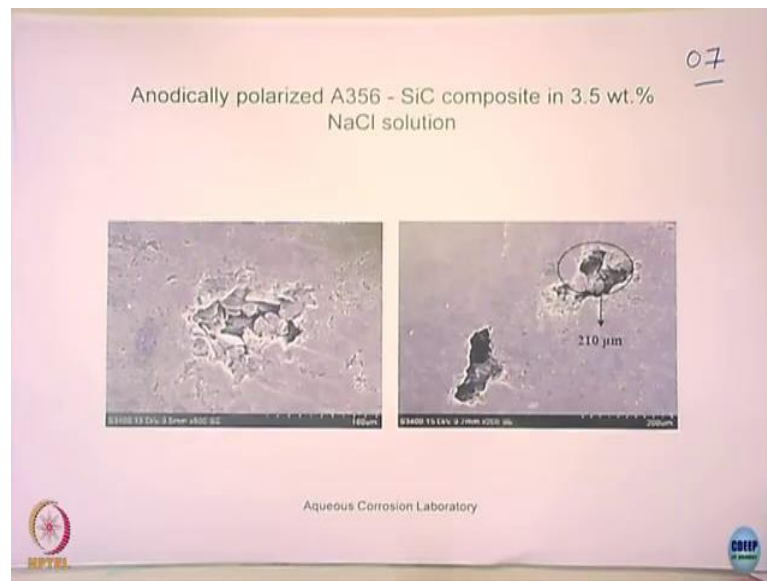
And they can start damaging. Sometimes the pit also can have a very complex morphologies, will see later actually. You can see here these pits, these are all corresponding to a stainless steel, where nickel was substituted with the manganese and why is people substitute nickel with the manganese? Because the manganese is cheaper and also, you can stabilize the austenitic phase.

So, it is equivalent of a 304 stainless steel, but very low nickel content with more manganese content. You see here, the pitting behavior is quite severe now. See this is

compare these two and you just see this the left side corresponds to the manganese substituted one actually, you replace nickel with that. It is going to nickel now.

Though this is the one with nickel is certainly far better compared with one replaced by manganese actually. Now, as I told you, the pits can be very complex, depending upon the microstructures. So, this is a slightly irregular morphology of the pit that you see here ok.

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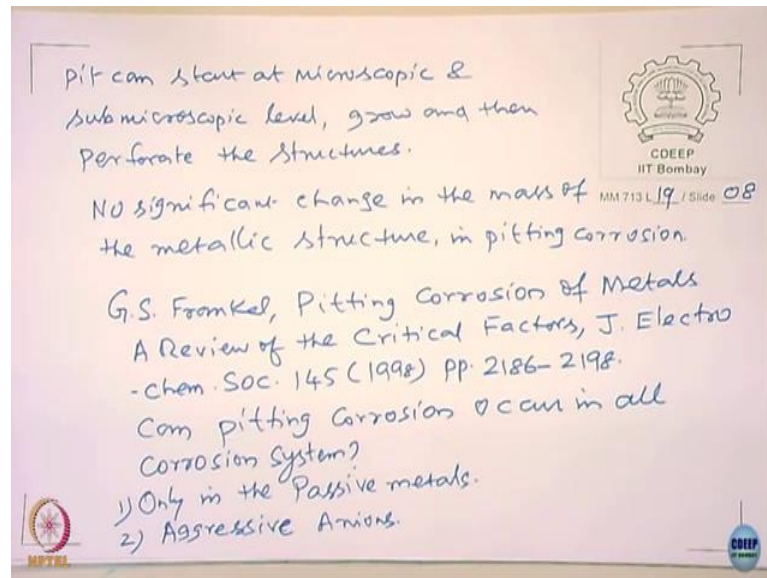


And this essentially, it is a composite right. It is an A356 aluminum alloy actually, wherein you had silicon carbide particles are added. This essentially used for the rotor disk for the auto gear applications the brake disc actually, its normally made up of cast iron, but cast iron are very high density. So, they want to substitute with aluminum; but then, aluminum is suffers very high severe I would say wear, wear problems.

So, what happens is they added with silicon carbide, the silicon carbide gives you good reinforcement and so, the wear resistance now. So, you can see that the pits are more complex. It takes the contour of some of these silicon carbides. Look at this shape of this, this follows the contour of the silicon carbon particles.

So, you can have a pit which it can be irregular pit based on the microstructure of the material actually. That means, the metallurgy also plays a very important role in pitting of the stainless pitting of the steels and other alloys.

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So, what we like to say is that the pit can start at microscopic and sub microscopy level. Then, grow and then, perforate the structures. That is why they are quite deleterious. Look at this corrosion at the microscopic level right that means, there is no significant change in the weight, change in the mass of the structures. So, there is going to be no significant change in the mass of metallic structure in pitting corrosion.

So, the test like mass loss test has no meaning right and why does it really originate pitting? There are lot of studies you know, there are probably hundreds of papers which are devoted to understand the pitting mechanism, pitting characteristics and so on and I do not think we have now the last word in understanding the pitting mechanism so far. Of course, a significant progress has happened in understanding pitting corrosion, but still there are several steps of pitting, we do not still understand.

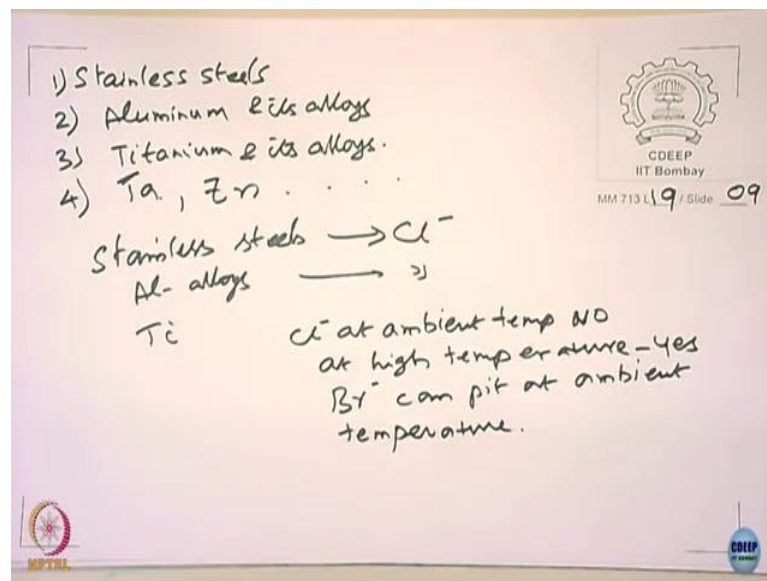
In this course, I am going to be a little brief. Because it is a first course and will not go into too much of science of the pitting corrosion, but however, if you are really interested to know to more, I would recommend strongly this article by G. S. Frankel. This article is a review and it is published in journal of the electrochemical society. It is a say a very good review ok, it covers quite a bit of fundamentals of pitting corrosion.

To start with, can pitting occur in all cases, in all corrosion system? The answer for that is it happens only in the passive system, in the passive metals. If the metals do not

passivate, there would be no pitting. Passivation is an important criteria first; the second, you need aggressive anions, you need aggressive anions.

So, even when the metal is passive, it may not pit unless there are specific aggressive anions. I give some examples. What are the metals which are passivating in wide environment? Stainless steels. Yes, then?

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Student: Aluminum.

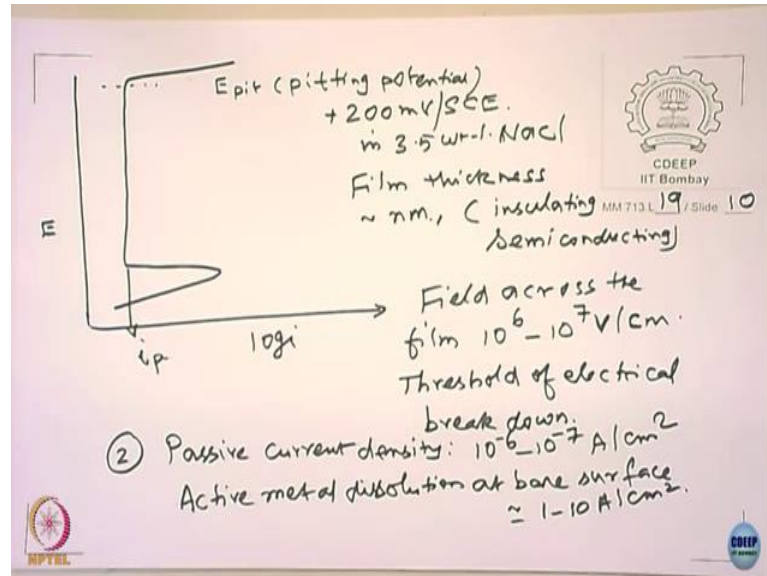
Aluminum, Titanium and its alloys. There are so many other metal like you have for example, you can have tantalum, and you know zirconium. You know there are several metals, which are passivating. It is also possible that you can passivate in pure iron and in a given pH conditions, you have seen the Pourbaix diagram. It is not necessary that stainless steels can passivate, in all cases not necessary. But predominantly, yes. From the engineering point of view, these metals, they exhibit passivation.

Now, all of them, they can undergo pitting. For example, stainless steels pit in chloride media, so as aluminum, titanium chlorides at ambient temperatures; at high temperatures, yes. But you can have like bromide for example, can pit.

So, passivation is an important criteria for pitting to occur and predominantly, these metals, they suffer pitting depending upon how severe the environment is and what kind of environment, it means the temperatures it means the nature of the anions that we if we

think about, in the both are included. As I told you, pitting corrosion is not so far well understood.

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Now, if you take a let us say if you consider a polarization curve, if you know of this, this is very familiar to you right and this is the potential, we call them as E_{pit} or also called as it is pitting potentials. Now, if you look at the voltage here, let us say a typically a 316 stainless steel in chloride medium maybe the E_{pit} could be about +200 mV versus saturated calomel electrode.

Pitting potential in let us say 3.5 wt. % NaCl solution. But actually if you look at the driving force for pitting, it is a very enormous. Now, what is this potential? This potential is with respect to the solution right, the potential of the metal with respect to the solution as measured by a?

Student: Reference electrode.

Reference electrode; in this case, a saturated calomel electrode. So, I am measuring the potential of this metal in relation to the solution, say 200 mV. But if you look at the film thickness, when I say film I mean the passive film thickness, they are in the order of nanometers. The metal is highly conducting this film, you can consider as approximately, you can say it is insulating or you may consider as a semiconducting in both you know.

So, it is a barrier for the flow of the current. Is it not? When I apply a voltage, the current is not rising. The current remains steady state here. This called a passive current density right. This is your i_p , passive current density because it is the film is offering a barrier resistance. But if the film thickness is in nanometers and even you apply let us say 0.2 V, what is the field across the film? The field across the film turns out to be about $10^6 - 10^7$ V cm⁻¹.

What is the field voltage by the distance or with the voltage is applied right. Now, look at this here. So, it is a very high field that means the metal is about to have an electrical breakdown, an electrical breakdown can happen. So, it is in the threshold of the electrical breakdown; one aspect of it.

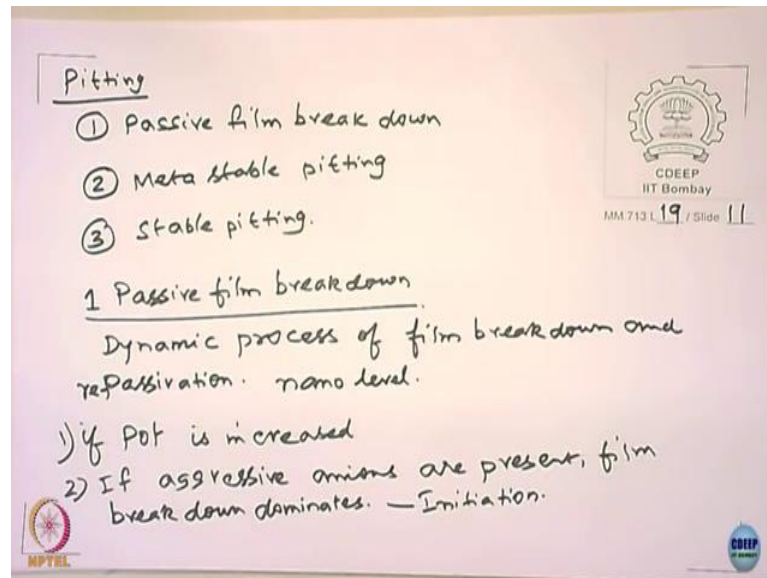
The second aspect of it is the passive current density is of the order of what? It is of the order of 10^{-6} to 10^{-7} A cm⁻². But if you look at the active metal dissolution at the bare surface, it is about 1 to 10 A cm⁻². Do you understand this?

The passive current density at these locations, you measure it; they are all in terms of microamperes. If the film breaks and if you expose a bare metal, the current density over here is the order of amperes; 1 to 10 A cm⁻². So, how many times the metal corrodes here as compared to the corrosion of metals in the passive state? How many times it is about? 10^6 about a million times corroding at higher rate.

So, if you look at the film breakdown, if due to some reasons, the dissolution at that location becomes very severe. So, rate of corrosion can be of the order of 10^6 , 10^5 depending upon what extent with bare metal is exposed. So, this pitting corrosion becomes very severe, very insidious and it happens at the microscopic level.

I hope I have conveyed the points clearly to you understand here. So, this is a very important type of failure, that is why a lot of work is gone, lot of research has gone to understand the pitting corrosion of metals.

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Now, let us look at the pitting. What it consists of? It consists of Passive film breakdown, then we called as Meta stable pitting, third we call them as a stable pitting. Let me explain to you what do I mean by these three events ok. These are the three events simplified events of pitting corrosion.

The passive film breakdown; now, let us take the case 1, now what do you mean by passive state? What do you mean by; so, what is happening in a passive metal. You get a definite passive current density, there is a film formation; but even then, there is a definite current flowing across the film.

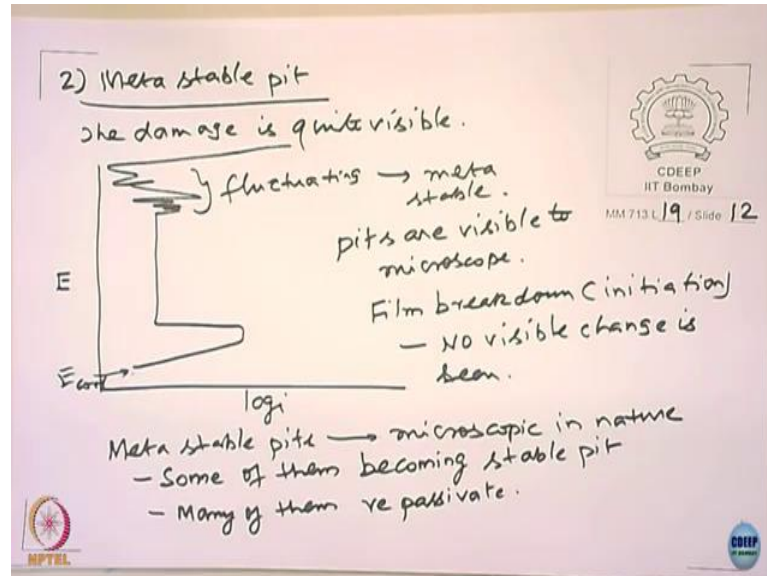
So, there is a metal dissolution, it is not that there is no metal dissolution. The metal dissolves, but dissolves at a lower rate. So, the passivity is it is a dynamic process of film breakdown and passivation, it continuously happens. The only thing is the rate of re-passivation, you use a term passivation may be more appropriate ok.

So, if we can quickly here and the current comes down ok. Now, they are all happening at nano levels. I want to say nano level it talk about spatial nanoscopic levels, specially they occur at the atomic and the nano levels, the metal atoms dissolve and there is a re passivation, are taking place.

But what can happen is if you rise a potential, the potential is increased. If the potential is increased or if some aggressive anions are present, film breakdown dominates. You may

call this as initiation. As I told you the initiation process is still less understood, the film is getting damaged, film is getting broken actually and the bare metal is exposed.

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When it is exposed, then what happens? It leads to metastable pit. You know what do you mean by metastable, anybody? It is between a stable and unstable state right; a stable state and an unstable state in between, the state is called at a stable state. It can again, you can either go to a stable state or it can move to a unstable state that is called a metastable state ok.

In the metastable pit, what happens? The damage is quite visible. Similarly, what do you mean by that? If you normally observe the anodic polarization curves of let say stainless steel, an aluminum alloys, some cases even titanium alloys, you start from the E_{corr} .

This is your E_{corr} and you rise the potential, you go to the critical current density, then passive state. Current apparently looks very stable current. When it start increasing, the current starts fluctuating and this is called as metastable place. Why I call a metastable here?

The pits are visible; pits are visible to a microscope, you just see them in the microscope, they can be of 1 micron or half a micron visible. As opposed to film breakdown, that is initiation process; no visible change is seen, you do not see them anything right.

In the other cases, you see that there is a dynamic process of metal dissolution and then repassivation taking place and see them in the microscope, you would not see any features. But over here, you observe in a microscope, you will see microscopic size pits appearing – disappearing, appearing and disappearing; that means, what it becomes truly metastable and some of these pits may become stable later.

So, you see metastable pit here ok, which are observable in the microscope and this metastable pits, pits are microscopic in nature. Some of them becoming stable pit and many of them repassivate, it goes to the original state of passivity.

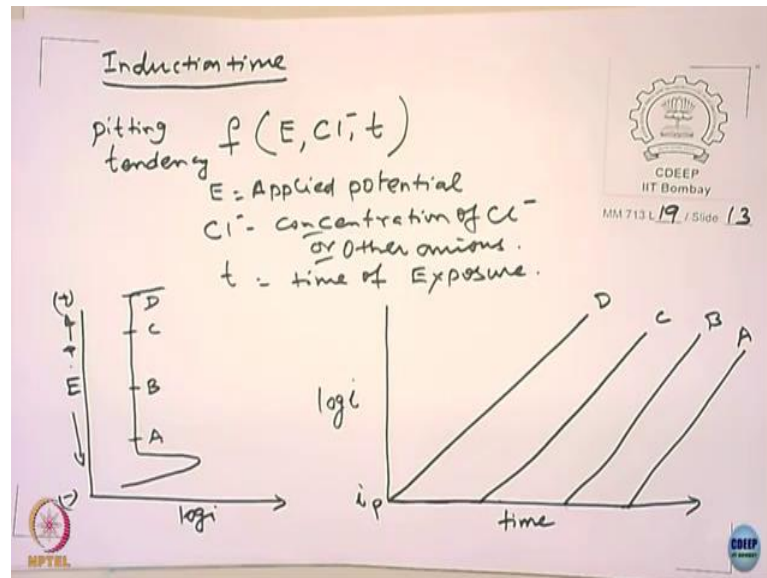
Now, what does it mean? You when you start moving from the corrosion potentials up towards the noble side, noble side you see the currents are fluctuating and then, the current becomes here. You will see here, what happens? Here, the current is steadily increasing and this becomes the stable pit. At this particular potential, it means stable pit.

So, called E pit, you describe is nothing but the pit that forms become stable; the pit does not disappear above that particular potentials and E pit and above, the chances of the pit remaining stable is very high; below the pit, the chances of pitting becoming stable become less. That it becomes the rest as you start moving down from here or so to say. It is possible to have a pit even at this particular place over here, over here, over here.

But what does really mean in real terms? In real terms the probability of the pit that is formed here becoming stable is so less compared to the probability of the pit so formed becoming stable. So, this probability is quite large here as compared to this. That means, the concept of E pit becoming a unique number is not correct. The pitting can occur below the pitting potential as well. At E pit and above, for sure the pitting will takes place. Hope I am making the point clear to you. So, the concept of saying that E pit corresponds to pit initiation is a little bit not a right terminology to use; all we can say is that yes, the pit will start stabilizing at their particular potentials.

So, this is something very important to look at it. In fact, this has lead to some concept of what is called as induction time.

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Actually, just to make some remarks, I would say pitting corrosion, pitting tendency is a function of applied potentials, the chloride or anion concentration. Then, the time is going to be other factors. E , where here E is applied potential, chloride is the here concentration of chloride or other anions, time is the time of exposure.

Now, if you take for example, let us draw this diagram of polarization curve, suppose like this. Suppose, you take these places, these points suppose you take and I hold the sample at that particular potential time versus the current $\log i$ you can call it $\log i$ current.

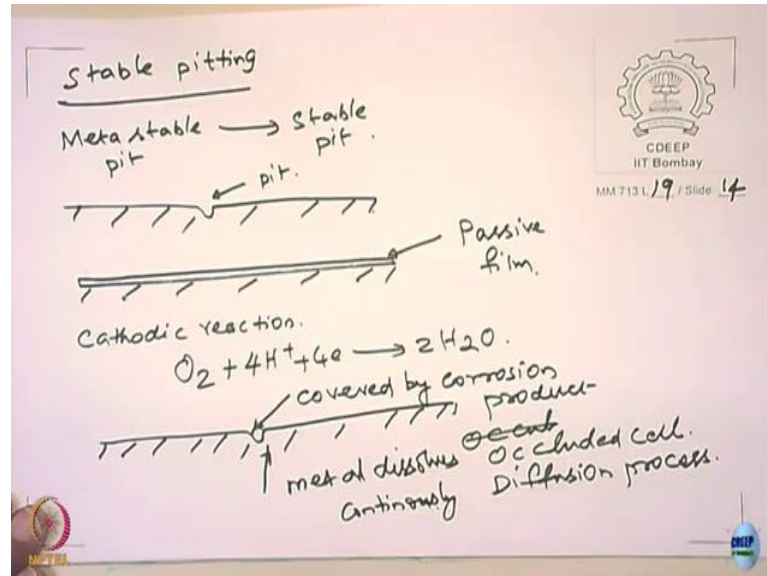
If I hold at potential corresponding to the point D, the current increases, D here. See what happens? This is your let us say this your i_p ; this current is the base current is i_p here. Here what happens? The current will remain here and then, this is going to be C; It is going to be B, it is going to be A here ok.

The increase in current corresponds to the pitting of the metal now just given some gross schematic here. Do not worry about the values. Just look at the relative positions of these current versus time curves. So, what does it mean? If you are going to hold it at D, the pit starts immediately, it does not take more time.

If you hold it and if you reduce the potentials, it takes longer time and so on B and, so as A right. So, which means that the chances of a metal pitting in your environment you

know it depends on what? It depends upon not only the potentials, also the time factors. So, this is something you should be looking at actually.

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So, now, the pit becomes stable. What makes a transition from metastable to stable pit? Here, there is a lot of similarity between a crevice corrosion and a pitting corrosion here. What makes the pit stable? The pit can repassivate that means, it can form the film; that means the pit becomes unstable or the pit will continue to dissolve and grow; that means, the pit becomes stable.

So, what makes this pit stable? Now, there are several theories are there, let us make it very brief and somewhat simple. Let us take a; let us take a surface. This is the passive film. The cathodic reaction and the anodic reactions, they occur all through. The cathodic reaction may be considered. Generally, for a stainless steel to passivate, the cathodic reaction has to be what has to be if it is an acid, if you are going to use be an acid.

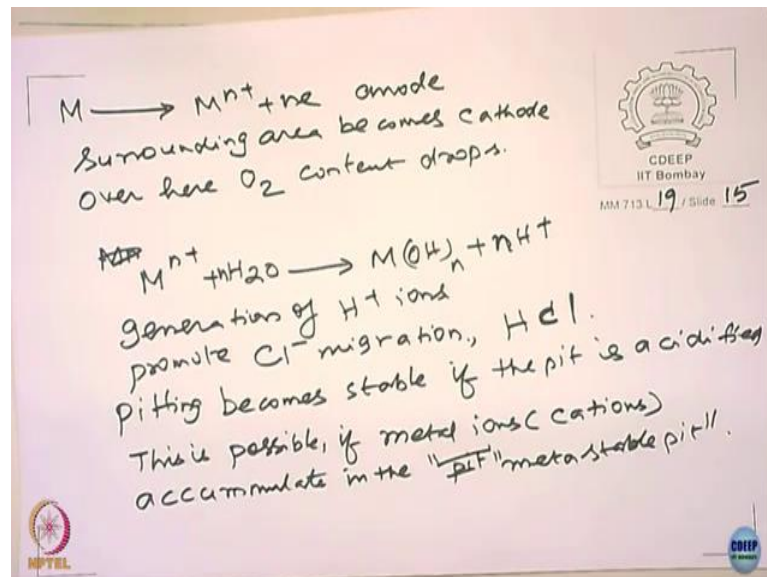
So, cathodic reaction is generally the oxygen reduction-reaction, then only it makes a potential in that passive region, otherwise you do not render the metal passive. You need to shift it to the passive region. So, the cathodic current, I mean sorry the cathodic reaction must have noble potential.

So, all through you have a metal dissolution and as well as the oxygen reduction reaction taking place, like this. Now, if there is going to be a pit formed, assume that there is a pit

formed. If the pit is covered by corrosion products, passive film whatever can happen; then, it becomes an occluded cell.

What is an occluded cell? The occluded cell, there is no convection; there is only diffusion process. So, it is only a diffusion process here. Now, in the pit the so called metastable pit, assume that it is a metastable pit, it is a metastable pit, there is a pit formed here. It is covered with some corrosion product or something, the metal continues to dissolve below this cover. Here, the metal dissolves continuously right. To dissolve continuously, it will generate various cations.

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For example, if you have M go into solution as $M^{n+} + e^-$, this becomes an anode. Now, the surrounding area becomes cathode and over here oxygen content drops. Why does the oxygen content drops? Because it is covered with the corrosion product. Now, you have this metal ions generated here and these metal ions, when they are generated, what happens now? You have now the generation of H^+ .

So, this also going to promote chloride ion migration, chloride or maybe iodide or whatever depending upon anions present in the electrolyte and they can migrate to this and it can form hydrochloric acid.

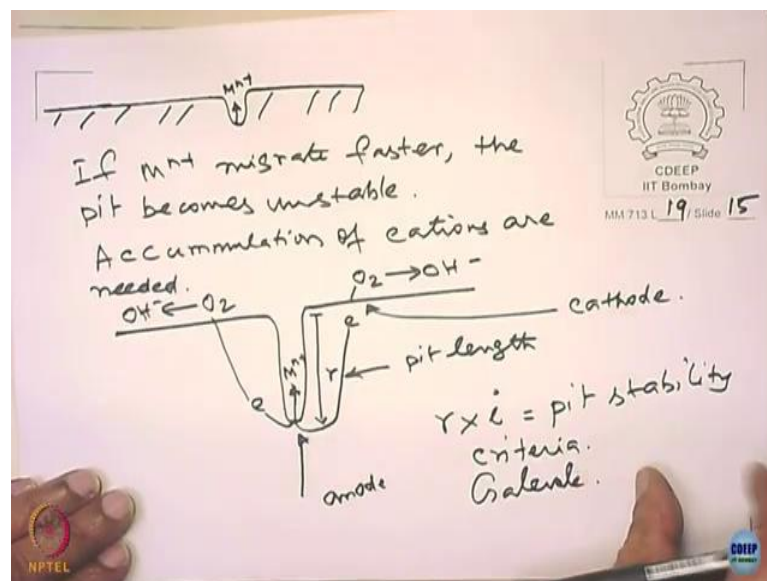
It is somewhat similar to crevice formation, am I right? Somewhat similar to crevice corrosion formation. Now, the question is when will the pit be stable? The pit will be

stable, if you form the acid. Pits become stable, pitting becomes stable, if the pit is acidified. How is the acidification is occurs? This is possible if metal ions or cations accumulate in the pit, or else in the metastable pit or occluded cells.

I hope you understand now. See here, you are not forming an external crevice. The crevice itself is formed by the corrosion process. Now, in order that the metal to dissolve continuously, that pit, the occluded location has to be acidified and should maintain that acidity.

Now, how is it possible? The acidity is possible is first of all created by it is created by the dissolution by the hydrolysis of the metal ions. Look at this the metal ions. It will interact with water, hydrolyze and form metal hydroxide plus H^+ . And H^+ in turn will attract more chlorides and form this ones. Assume that this metal ions can easily migrate outside. I have a pit, your metal ions they just go out of the surface, what will happen?

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So, here is the metal ion that are coming here, metal ions are formed here right. Assume that these metal ions do not get accumulated, they just go away from the surface, get into the electrolyte. So, what will happen? Increase or decrease?

Student: Decrease.

Why would decrease?

No, you are right; pitting will not occur. Why it is not happening? No, what does the metal ions first of all do, if they stay here, what do they do?

They form?

Ions right. They form hydrogen ions, they hydrolyze. If these ions are quickly moving away from the surface, what will happen to acid formation?

Student: Reduces.

The acid formation reduces, the chloride ion migration also reduces and so, the pit becomes unstable. So, if M^{n+} migrate faster the pit becomes unstable or I put other way around you need. So, to say accumulation cations are needed. If they are not accumulated, they are washed away from the surface. Now, a pitting will not be stable that surface becomes again passive.

Now, let us look at this. I made this little bit longer; this is the "r" length of the pit or is the pit length. Now, please look at here, the metal dissolution occurs; the electrons will travel here and they may combine with oxygen and you can form hydroxide.

Electrons also can travelled here, combined with oxygen here and you can and it can form hydroxide water whatever you can form. So, you have an anode here and here you are going to have a cathode. I think most of you are engineers now, right.

I am going to put a question to you. I want more cations to be here because when I have more cations, it will hydrolyze and form acid. It also can lead to migration of chloride ions in the pit. Now, what makes; now look at there, there are two processes; one is the dissolution of the metal ions giving rise to this.

What is the other process? The other process is the migration of these ions from the pit to the outside the pit. So, now you tell me, what are the governing factors that will make the pit stable?

Student: Gravity.

Of course, gravity is one thing. Assume the gravity is there ok. Gravity is going to be everywhere now. What are other factors in terms of pit dimension, the other one?

Student: Depth of the pit.

The length of pit and the rate of dissolution right. So, the product r , length of the pit and i , the dissolution current is a parameter used to describe the pits stability. Please look at they are multiplied; if r is higher, I can have a lower current density. Why? Because diffusion path is longer.

If the diffusion path is shorter, then I must have a higher dissolution rate in order to make the pits stable. So, the pit stability, this is the criteria I used by a great guy called Galevalle. So, this is one of the important criteria in deciding whether the pit formed in a metal will happen or not.

So, I think I will not get in too much of things beyond this particular point actually ok. Only one thing, I want to make a mention that I think is important that probably you like to know and then, you move on to with respect of that.

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$Al^{3+}, Fe^{2+}, Cr^{3+}$
they produce different pH.
 $K \quad Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+$
K.

Summary
Pitting corrosion occurs in passive metals.
Film break down and localized corrosion
causes pitting.
Meta stable pitting, can occur even below
E_{pit}.
pit stability depends on the pit chemistry.
pit chemistry → diffusion parameters:
Cation accumulation.
 $r \times i$.

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Now, there are various metallic cations; let us say aluminum, iron Fe^{2+} , Fe^{3+} whatever, you may have let us say chromium. So, very interestingly that each cations they produce different pH that is decided by the K value. For example, you have Al^{3+} water K value. K for that will decide what can be the pH. So, those ions will use acid, it is acids. Anyway, let us not worry too much ok.

So, the criteria of pitting is this. So, to summarize what we have seen so far. Pitting occurs in passive metals. Film breakdown and localized corrosion causes pitting. Now, you have a criteria called metastable pitting, which can occur even below E_{pit} ; it can occur even below the E_{pit} . Pit stability depends on what? Depends on the pit chemistry right. The pit chemistry is not promoting, it is not good enough, then pitting will not occur.

So, the pit stability depends upon the pit chemistry and pit chemistry in turn depends on what? Pit chemistry depends upon, depends upon the diffusion parameters which means cation accumulation right, which is it defined by the criteria called $r \times i$. So, please go through this, I mean and we can discuss this.