Aqueous Corrosion and its Control
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Lecture – 20
Forms of corrosion: Pitting Corrosion (Part – II)

Discussing the topic of Pitting Corrosion; in the previous class we discussed the fundamental or the basic mechanism of pitting corrosion. We saw that the pitting corrosion essentially occurs in what metals? The metals exhibiting the.

Student: Passivation.

Passivation. So, that is an important criteria. The second criteria is that the pitting corrosion occurs in selective environments actually. You must have a species that should induce pitting corrosion. This is the second important factors.

Then coming to mechanism we said that the pitting corrosion mechanism can be considered as pit initiation, metastable pitting and then a stable pit growth. The understanding of the pitting initiation is not still well understood process. We saw that the factors that cause the pit initiation or you say the applied potentials which will break the passive film. The breakage of the passive film is assisted by the environment like chlorides and all kind of things.

And, but then when you start initiating that when the film breaks down occurs it is not guaranteed that wherever the film has broken will lead to ultimate pitting. There will be always damage of the film, the repassivation of the film; they occur in a dynamic manner actually that we call it as a metastable pitting. Of course there is a damage to the metal, if you observe microscopically there are sub microscopic or macroscopic level pits are occurring, but these pits not necessarily stabilized.

Thus we looked at the stabilization criteria. The stabilization criteria for the pitting is what? It is that the pit has to have it is own chemical environment, that chemical environment must be in acidic; it must have also rich in the damage causing species such as the chlorides. So, whether the pit will be stable or not depend upon how good you may able to stabilize the environment within the pit; outside the pit you are going to have a normal chemistry what is taught with actually, within the pit it is an occluded cell.

Now, there are dynamic processes the metal dissolves, it releases cations actually. They go from the pit surface to the pit. From the pit the metal ions migrate outside the pit, goes outside the mouth of the pit right. If they stay within the pit they hydrolyze giving rise to what is called as H^+ ions that also leads to the migration of the chloride ions because of maintaining the charge neutrality; H^+ means more positive; so, the cation hydrolysis which decides the pH of the environment.

So, there are two processes; the dissolution process and the migration process that is why we said the criteria for pit stability is radius multiplied by the i that is the criteria that the pit could be stable or not. Now, of course, we can go in deeper in studying the pitting mechanisms and you know various factors. I think since it is your first course on corrosion we will not go into depth on the mechanisms.

Now, what we are going to look at today? Two aspects; one is the pitting characteristics and the factors that control pitting corrosion of the metals. What are the governing factors? The second aspect of that is how do we control the pitting corrosion and how do you evaluate at a test a material for pitting corrosion? With that I think we will be completing the discussion on pitting corrosion of metals.

So, let us look at the when do you call a pit, you have uneven corrosion occurring on the surface right. In fact, most uniform corrosion that you see are uneven. We can usually see there are rough surfaces. You see industries, when you go the steel surfaces are covered with the oxides; ferric oxide. You remove it you see surfaces have undulations now people mistake it as pitting corrosion. Now, you should be able to define when you call that surface undulation as the pitting.

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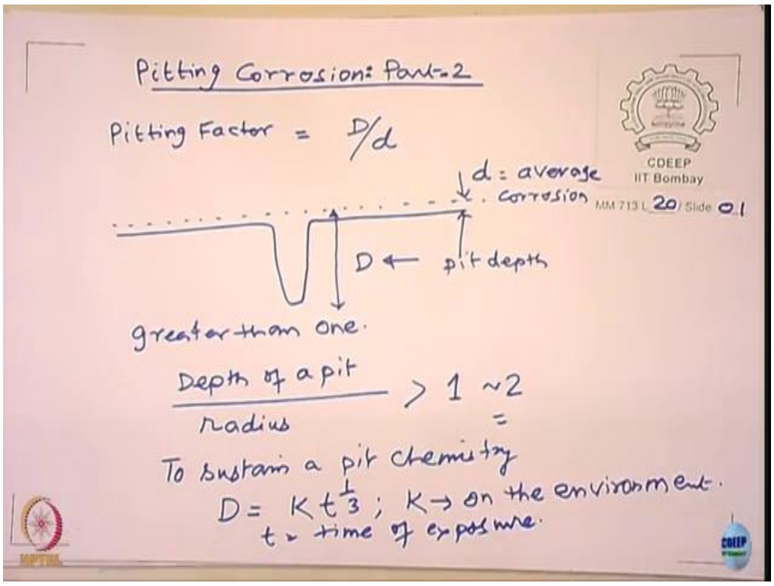

Pitting Corrosion: Part-2

Pitting Factor = D/d

d = average corrosion

$D \leftarrow$ pit depth

greater than one.

$$\frac{\text{Depth of a pit}}{\text{radius}} > 1 \sim 2$$

To sustain a pit chemistry

$D = K t^{\frac{1}{3}}$; $K \rightarrow$ on the environment.

t = time of exposure.

The one of the criteria is called as a pitting factor. The pitting factor is given by and before I do this I draw this diagram of corrosion gives you pitting. This is a pit you see here right and there is also uniform corrosion occurring on the metal. This is the d, average corrosion- uniform corrosion you may call it and this is the depth over which the pit has occurred D, this is the pit depth.

Now, the pitting factor is given as D upon d is a pitting factor. So, it should be greater than 1, then you call a pitting; if it is not greater than 1, you do not call it as a pitting. The other way of defining the pitting is it should be depth of a pit upon the radius. When I say radius it is a gross radius you are not going to have a perfect circle right ok; perfect in a spherical this thing ok. It should be you know I think some people define it you know it should be greater than 1; some people call it as 2.

So, you have very shallow kind of thing you know, then it is not pit. Now, this makes sense right. If the pit radius is very large and the depth of pit is very small, what happens? Can you connect it to the mechanism?

It is not crevice corrosion; the migration becomes much easier right? It is no more a diffusion control and you can subject it to convection right if it is. So, shallow the metal will just get out of the pit, it would not sustain a pit chemistry right. So, this is to sustain a pit chemistry, so that the pit becomes very stable. The people also have been following the pitting kinetics of various metals and some people have come to this kind of relationship. The pit depth there is related to K times t to the cube root you, add this thing and D means the depth of the pit right and K depends upon what? K depends upon the environment.

Please understand this is related to growth data, it is not related to pit initiation. The pit initiation may take weeks, it may take a month, it may take an year whatever. But, this only talks about the pit growth; it does not talk about pit initiation. What is t here? The t corresponds to the time of exposure. It is necessary to understand the pit is not only one shape you can have a complex shapes, you can have a different morphology of the pits ok. So, it is necessary to recognize that actually.

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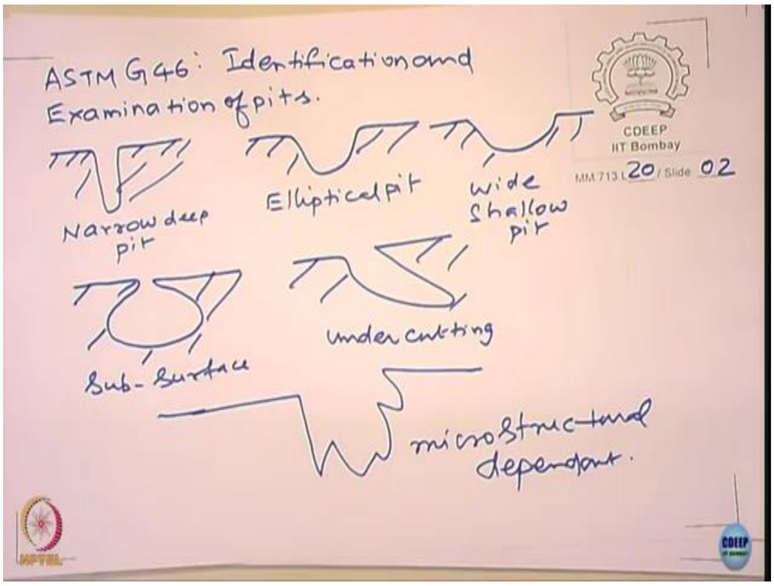

ASTM G46: Identification and Examination of pits.

So, we see that you know there can be different morphologies of the pit and if you want to know more details you can look at this the standard ASTM G 46. It talks about identification and examination of the pits. It talks about various pit morphologies. I just reproduce some of them here schematically right.

And, let us say you have it is called narrow deep pit. You can have elliptical pit. You can also have wide shallow pit. You can have pits which are sub-surface. You see here it is just undercuts, just sub surface pits it grows like a internally it grows like that you know.

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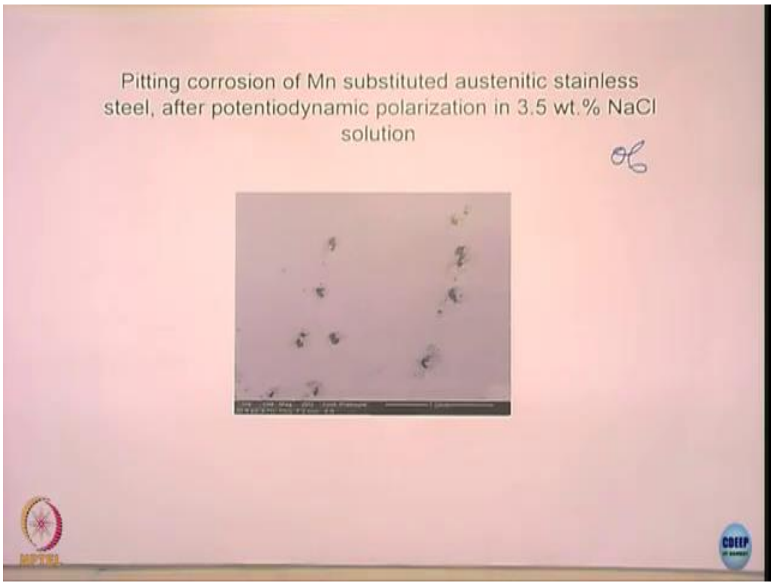

Pitting corrosion of Mn substituted austenitic stainless steel, after potentiodynamic polarization in 3.5 wt.% NaCl solution

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And, there are some see if I have some photos. Yeah, the some examples of how it goes I suppose you will able to see this. This is a pit here and pit has grown sideways and you know from the bottom start corroding up and so, you see the pits here very fine pits. So, you see a small corrosion and there is a lateral corrosion taking place right and from the bottom it just starts corroding.

And, ultimately leading to this kind of morphologies. You see this kind of things could happen in this systems you also see a similar things here.

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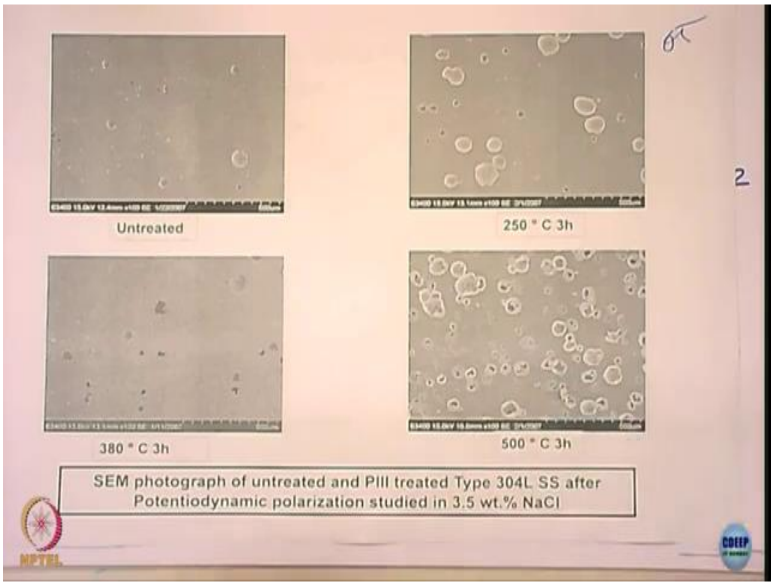

SEM photograph of untreated and PIII treated Type 304L SS after Potentiodynamic polarization studied in 3.5 wt.% NaCl

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These are all corroded and then lifted see about a lift here, it is just about to lift here. So, these are the portions you know I hope you are able to see this here look at this and it is corroded from the bottom and moves up and then it just goes away. So, you can have a very complicated pit morphologies, it can happen.

You can also have sometimes very strange undercutting. Sometimes it follows the microstructures, if suppose you have some zag follows all kind of things microstructural dependent. It just takes the takes the shape of microstructures I think I have shown this in the beginning of the earlier class, let me just see if I can fish off that slide yeah you can see here right.

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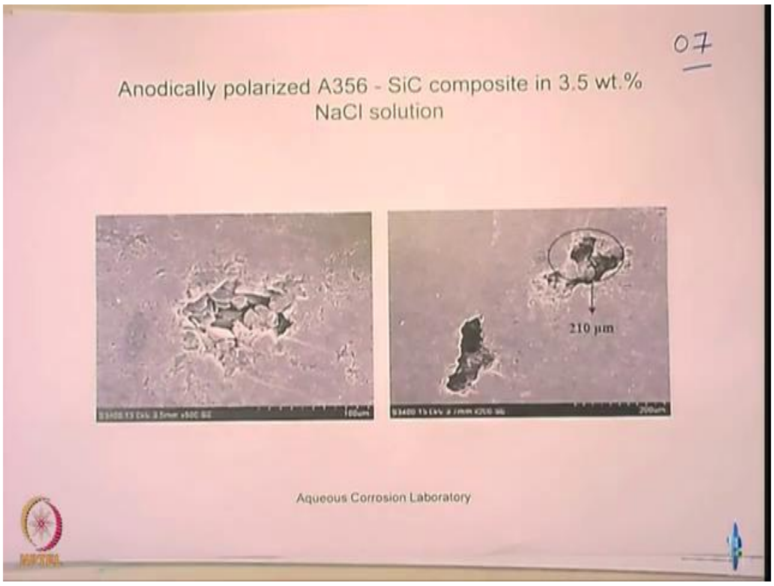

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Anodically polarized A356 - SiC composite in 3.5 wt.% NaCl solution

Aqueous Corrosion Laboratory

These pits are all taking the morphology of, this is a composite see you can call it by composite and. So, the shape of the composites are taken here. So, it can take all kind of complex shapes. So, you can have a nice hemispherical pits and you can have complex shape pits depending upon the alloy; because alloy is not homogeneous all the time. It can be chemically heterogeneous and so, there can be uneven type of corrosion morphologies or pits.

Now, let us look at the factors that control the pitting corrosion because if you understand the factors controlling pitting corrosion, then you can able to prevent pitting corrosion.

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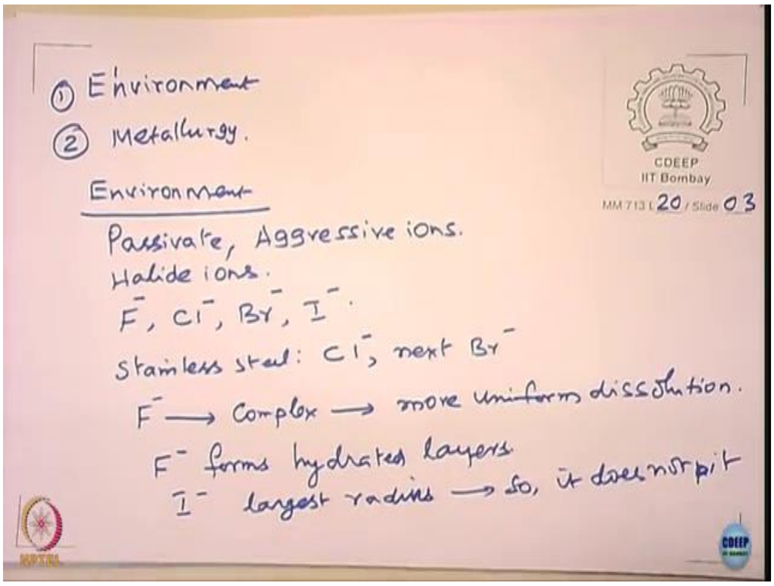

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① Environment
② Metallurgy.

Environment

Passivate, Aggressive ions.
Halide ions.
F^-, Cl^-, Br^-, I^-.
Stainless steel: Cl^-, next Br^-
F^- → Complex → more uniform dissolution.
F^- forms hydrated layers
I^- largest radius → so, it does not pit

Broadly, I would like to say that there are two kind of factors; one related to the environment and the second one related more to the metallurgy. Let us look at these factors briefly. Let us look at the environment. You have seen the condition it should passivate right, should have aggressive ions. Mostly the halide ions are considered to be aggressive. What are these halide ions? Anybody? Do you remember what are they?

They are fluorides.

Chlorides, bromides and iodides. When it comes to stainless steels, the most aggressive is chloride, next is bromide and the fluoride, and iodide they are not really that aggressive. So, broadly speaking I would say not actually one can verify all these parameters.

Fluoride, see if you have passive film; if the passive film has to get damaged by these ions, ions have to migrate in the passive films right. They have to migrate and then form a complex all of this is possible. The migration depends upon what? The radius of the ions. If the radius of ions is too big, then migration becomes very difficult.

So, if you take it that way fluoride is ionic radius should be smallest as compared to chloride and bromide and iodide, but even then the fluoride does not cause severe pitting as compared to chloride for two reasons. One – the fluoride forms complex and so, promote more uniform dissolution. The second reason is the fluoride forms strong hydrated layers.

See, these ions in water are not very free, they are hydrated. The water molecules you know I mean these ions are enveloped by the water molecules; even you take H^+ ion they are not free ion. H^+ ions are covered with what? Covered with water molecules. Why? Water is a polar molecule right, it has got a positive charge and negative charge and so, they get enveloped.

So, when you have a fluoride it is getting hydrated, it is very strongly hydrated then it would not allow the water to come out and free the fluoride ions because to remove the water molecule from the fluoride ions are more difficult because the charge density is more on fluoride as compared to the chloride. So, the two reasons make the fluorides less aggressive towards pitting as compared to the chlorides. And, iodide is the largest radius so, it does not pit does not cause pitting rather actually.

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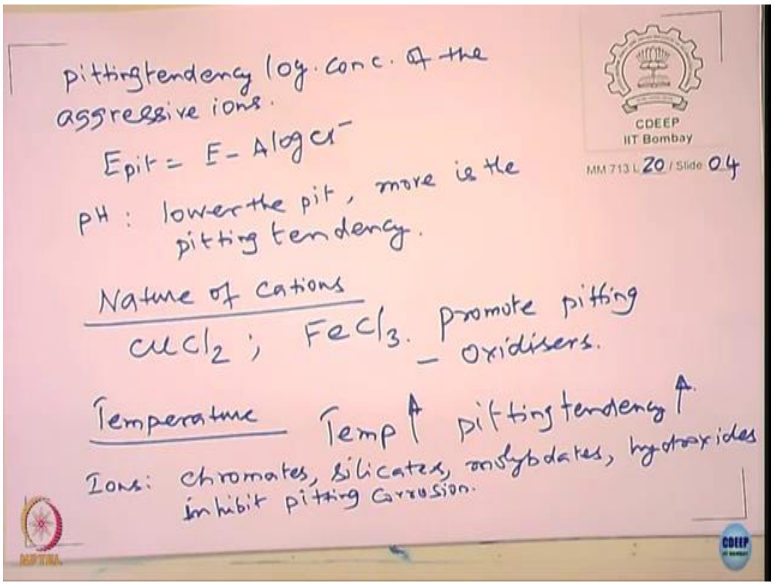

pittingtendency log. conc. of the aggressive ions.

$E_{pit} = E - A \log Cl^-$

pH : lower the pit, more is the pitting tendency.

Nature of cations

$CuCl_2$; $FeCl_3$. promote pitting – oxidisers.

Temperature Temp ↑ pitting tendency ↑.

Ions: chromates, silicates, molybdates, hydroxides inhibit pitting corrosion.

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Now, there is a kind of empirical or thumb rule that the pitting tendency is logarithmically related to the concentration of the aggressive ions. Something like you can say Epit = E - A log (chloride ion) something you can say that. So, the E pit will decrease if you increase the chloride ion concentrations; A this factor depends upon the nature of the aggressive ions. So, higher the concentration of chlorides and more susceptible they are towards pitting.

It also depends upon the pH ok; lower the pH more is the pitting tendency. What happens now, it is easy for the pits to stabilize in acidic pH. You have H^+ ions in the solution. You also have one more thing that is the nature of the cations. Suppose, I add cupric ions, I add ferric chloride ions for example, ferric ions. So, what do you think will happen to the pitting?

When I add the ferric chloride let us say I have taken stainless steel and immersed in sodium chloride solution and maybe it has taken 6 months to pit right, 304. When I add ferric chloride what do you think will happen will the time for pitting will increase or decrease or you do not want to change at all? Can you remember some time back I gave an empirical you know relationship that E pit is a function of what? function of chlorides, time and of course, the applied potentials right. The pitting tendency I said that these are function of applied potentials, concentration of the species, the time of immersion right.

Now, when I add a ferric chloride what happens? What do you think will happen, any idea? What is the nature of ferric chloride? What is that you are associating ferric chloride? It is oxidising species right the standard potential of ferric and ferrous ions equilibrium is quite positive right. So, when I add these ions what happens? What will happen to the corrosion potential of stainless steel in sodium chloride solution? What will happen?

Student: It goes up.

It will go up right. So, when the potential goes up what will happen to tendency of pitting?

Student: Increases.

Increases right. So, when you add this ferric ion these are oxidizers so, they promote pitting. Because they are all oxidisers on the other hand suppose I add let us say you know sodium chloride or nickel chloride you know they are not really going to change the potential of the electrode potential of the corroding metal, they may not have very significant effect on pitting corrosion.

So, what about the temperatures? What you think will happen to pitting corrosion? When the temperature increases so, what will happen to pitting corrosion? Diffusion becomes positive, what more can happen actually. That is only one aspect of it. What also happened to the dissolution of the metal ion or the pit.

Student: Increase.

Increase right. So, it is going to increase. So, raise in temperature, when the temperature is increased pitting tendency also increases. In fact, they are also make some of the salts formation and the salts and then it stabilizes the lower pH and stabilizes the chlorides. So, raise in temperature is always detrimental towards pitting corrosion.

Now, some of these ions say chromates, silicates, molybdates and even we add hydroxides they inhibit pitting corrosion. In fact, for aluminium alloys to improve the pitting tendency they give conversion coatings. They give you conversion coating with chromates. The chromates indeed promote resistance against pitting corrosion of aluminium alloys.

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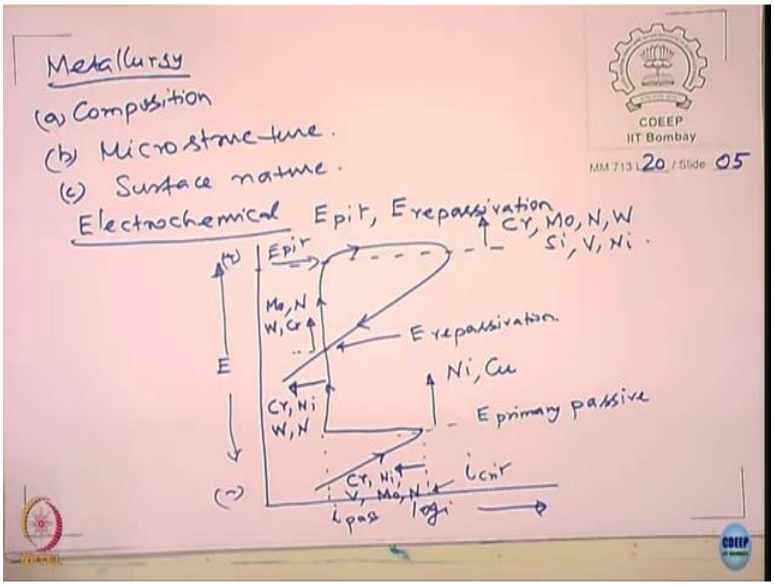

Metallurgy

(a) Composition

(b) Microstructure.

(c) Surface nature.

Electrochemical Epit, Erepassivation

Let us look at the metallurgy. Here we are not going to look at most of materials say titanium undergoes pitting and almost all passive metals will undergo pitting given the conditions. So, we will just confine mostly towards stainless steels very broadly used actually ok. So, let us look at the metallurgical aspect of it when I say metallurgy we say the composition, one aspect; 2 – the microstructure right. You can also talk about the surface nature, is not really metallurgy that is say that way surface nature.

Now, let us take the case of stainless steels and discuss these aspects in details because stainless steels are very widely used and they are prone to pitting corrosion. What are the constituents of stainless steel, anybody?

Of course, base alloy is iron, you have nickel, you have chromium, you have molybdenum, sometimes people add nitrogen, they add tungsten, they add copper and you know, and sometimes you can add manganese kind of stuffs silicon for example, they add actually.

So, let us look at how these alloying elements affect the pitting tendency of the metal. Now, the pitting tendency of the metal you can define by some electrochemical parameters right. What are the parameters, anybody recollect? What are the parameters that you can use to measure the relative resistance of an alloy to pitting?

Student: Pitting potential.

Pitting potential and other one is called as the repassivation potentials ok. Now, let us look at this how various alloying elements affect this these two properties. So, schematically this is the forward scan, backward scan right. From the corrosion potential you rise the potential you get what is this called. This is called as, what you call this current density?

ic, i critical current density and what this is called.

Student: ip.

i passive and what is this one? E pit and this is called as E repassivation potentials.

Now, let us look at the elements that can affect this. The elements that move up the E pit are going to improve the pitting resistance of the stainless steels. So, what are these elements? These elements are chromium, molybdenum, nitrogen, tungsten, silicon, vanadium and nickel. So, these elements they increase the pitting potentials. So, when you increase the pitting potential; that means, the initiation tendency of the metal to pit is reduced.

What about this? It goes up, it is good. It is called repassivation potential; it is goes up. These things you have molybdenum, nitrogen,

Tungsten and chromium. Of course, you want to know about the passive current density if you want this to be reduced or not, the passive current density is reduced these elements – chromium, nickel, tungsten and nitrogen to a certain extent. And, you want to know about this one, what is this potential called? E primary passive potential right.

What are the factors that affect this? And, see nickel is not good it increases and so, as copper it increases. Which one decreases this ic? Now, these elements like chromium, nickel, vanadium, moly and nitrogen. So, in fact, this forms a basis for development of various types of stainless steels which are resistance to corrosion in general, pitting corrosion in particular, crevice corrosion in particular and this forms a basis of that.

Of course, you know you cannot keep adding into the way you want, suppose I take a austenitic stainless steel I want to increase the pitting resistance I cannot keep adding so much of chromium right. When we add it, what happens? The austenite phase will turn into a ferritic phase. So, then you need to make a phase balance. So, you need to add nickel to it right.

So, the alloy development is a different story all together right, but the corrosion resistance story depends on this diagram and in order to get different phases you compensate with the relevant alloying elements ok. So, that is a different story of physical metallurgy of stainless steels, we will not be discussing over here.

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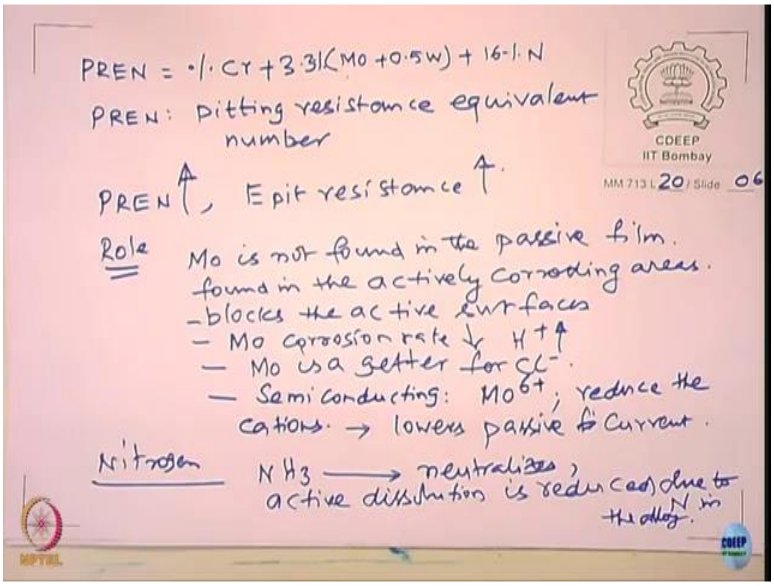

$PREN = \% Cr + 3.3 \% (Mo + 0.5 W) + 16 \% N$

PREN: pitting resistance equivalent number

PREN $\uparrow$, Epit resistance $\uparrow$.

Role Mo is not found in the passive film.
found in the actively corroding areas.
- blocks the active surfaces
- Mo corrosion rate $\downarrow$ $H^+ \uparrow$
- Mo is a getter for Cl^-.
- Semi conducting: Mo^{6+}; reduce the cations. $\rightarrow$ lowers passive film current.

Nitrogen $NH_3 \longrightarrow$ neutralizes, active dissolution is reduced (due to N in the alloy).

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Now, if you look at here, there is also an empirical equation. So, to correlate alloy chemistry to pitting corrosion that is using PREN, is an index which is given as Cr (chromium) % + 3.3 (Mo (molybdenum) % + 0.5 W (tungsten) %) + 16 N (nitrogen) %.

What is PREN? Is called as pitting resistant equivalent number. And, you can say that if PREN increases, pitting resistance increases. So, for applications involving large amount of chlorides like sea water applications, the stainless steels with higher PREN are being developed some of the in fact are in use ok. Now, I give some example here.

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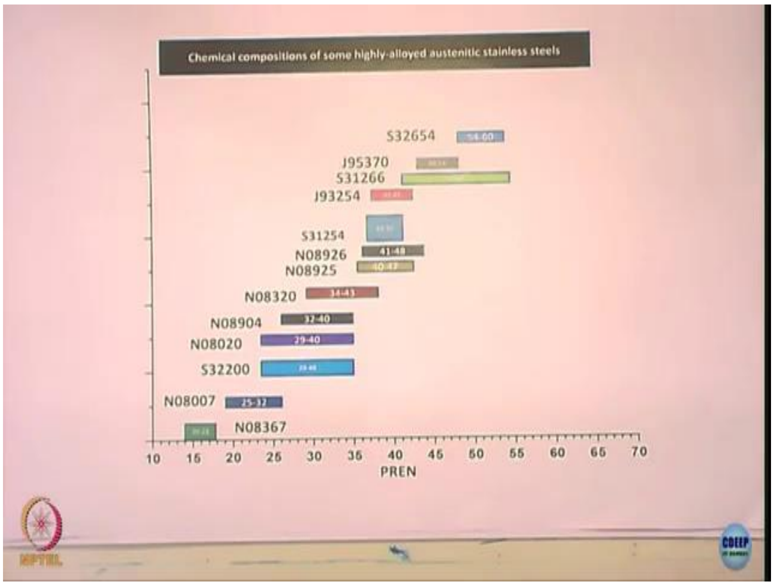

Chemical compositions of some highly-alloyed austenitic stainless steels

I hope you can able to see this chart here. This represents various austenitic grade stainless steels you can use this kind of things for even ferritic grade also you can do that.

What is given here is the PREN number you know starting from let us say 15 right is going up to let us say 60 and see the stainless steels have been developed starting from here up to this right. This called as 654 SMO. This has got a 6 molybdenum is higher amount of molybdenum is present here.

Now, you cannot add high amount of molybdenum because it becomes a ferritic stabilizer. So, people add more amount of nickel to that actually. So, this is also you have 254 SMO. This 254 SMO this and 25 chromium you have actually.

So, the various kinds of stainless steels are being developed in order to have higher pitting resistance which means they do have higher PREN number, but the cost of this also going to go high. You have more nickel more molybdenum it is really increasing it is cost of it that is one of the problems of using austenitic grade stainless steels.

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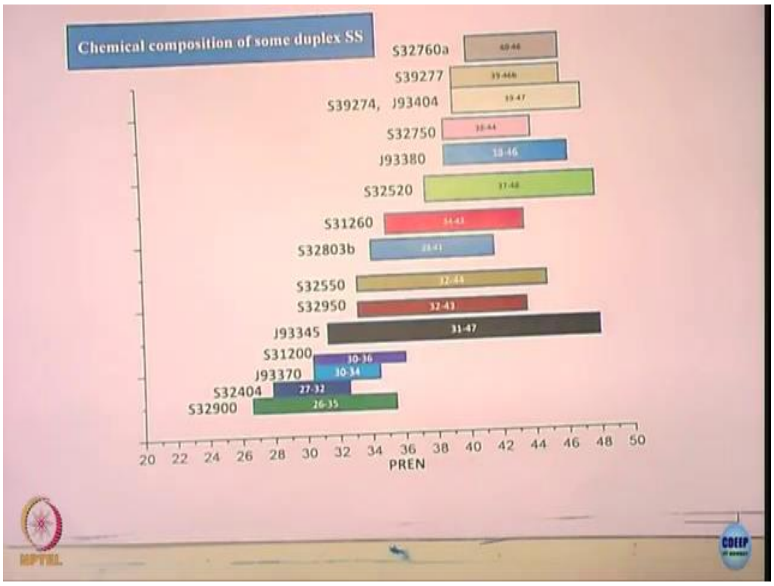

Chemical composition of some duplex SS

So, what happened was that there is a variation of this. People use what is called as a duplex grade stainless steel it is somewhere in between nickel based alloys and the nickel based alloys also have very high pitting resistance.

Now, the cost of the duplex stainless steels with high PREN number are lower compared to the cost of austenitic stainless steels with high PREN number. The reason is very simple the nickel content in duplex stainless steels are all going to be mostly lower compared to nickel content in the austenitic grade stainless steels.

So, again there is a gradual growth of duplex stainless steels with low PREN number it going up to 40 – 46 and so on. Now, look at this duplex stainless steel can be used in seawater application where the chloride content is 3.5 wt.%. Similarly, you can also use 654 SMO you can use that, but then this is really very expensive this material here compared to the duplex stainless steel here.

So, what I am trying to say is that the development of stainless steels were based on understanding the chemistry of the alloy towards the pitting corrosion of the metals actually. In all these the nitrogen plays a very significant role. Let me just see if I can show you some kind of curves here.

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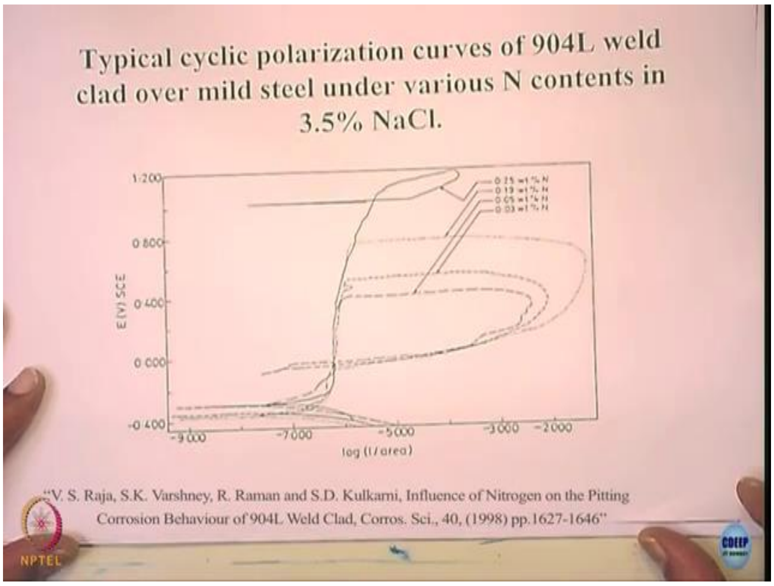
Typical cyclic polarization curves of 904L weld clad over mild steel under various N contents in 3.5% NaCl.

"V. S. Raja, S.K. Varshney, R. Raman and S.D. Kulkarni, Influence of Nitrogen on the Pitting Corrosion Behaviour of 904L Weld Clad, Corros. Sci., 40, (1998) pp.1627-1646"

Let me show this polarization curve and see, it is essentially a 904L filler wire. You know what is called a cladding, right? What is the cladding, you melt and deposit you can also deposit without melting also actually, right. It is a layer of in this case 904L formed on mild steel here. This is done by welding by weld cladding. So, you melt it and apply on this and the mild steels this is 904L.

So, what happens, see in this case the carbon steel why people go for cladding? Because you want to go for higher corrosion resistance materials and going to have a thick one it is very expensive right.

So, you can go for a carbon steel or other steel having lower cost, go for a thicker component you just deposit a clad layer of let us say 2 or 3 millimetres that takes care of the corrosion and the basic substrate takes care of the strength characteristics. So, it becomes cheaper.

Now, we have done some work related to 904L. Look at this here it starts with, this is the 904L without adding any nitrogen. When you start adding nitrogen further and further you see what happens now? The pitting potential increases and even the repassivation potential also increases. Now, in this case the nitrogen content is 0.25. So, when added to the weld, more nitrogen what happens the pitting resistance increases significantly please see here the rate is about 0.25 wt.% only, is not too much.

So, by adding this nitrogen you can increase pitting resistance from E pit value from minus 400 it is gone up to 1.2 volt. In fact, 1.2 volt means it is not pitting actually if you look at the Pourbaix diagram it will be what? It will be oxygen evolution reaction.

So, essentially this does not pit at all by just addition of small amount of nitrogen. So, all development can be done to improve the pitting performance of stainless steels because pitting corrosion also is very widely studied from the mechanistic point of view.

What I mean by that? When add molybdenum, when you add molybdenum, when you add nitrogen they are much more effective as compared to chromium actually.

So, people have studied why molybdenum is very effective, and people studied why nitrogen is very effective because there is no last word right still there are multiple theories as to why molybdenum improves pitting resistance as to why the nitrogen improves pitting resistance.

I just summarize a few of that and then move on to the next topic. The role of molybdenum has been, first of all they say that molybdenum is not found in the film, not found in the passive film. It is found in the actively corroding areas.

So, suppose you have a pit. In the deep of the pit you can find molybdenum or you are going to keep the metal in the active region and then you observe the surface will have more molybdenum. But, in the passive region the passive film there is no molybdenum at all and so, this led to some kind of understanding that the molybdenum- it says, it blocks the active surfaces; so, one kind of hypothesis really.

There is also other hypothesis which says that the molybdenum corrosion rate decreases when H^+ concentration increases. It is a very uniqueness of molybdenum actually right you saw before when the pH of the environment decreases what happens to corrosion rate? Increases, right? But, molybdenum has a different characteristics.

When you increase the acid concentration, the corrosion rate of molybdenum decreases; this is called as a negative reaction order. Suppose, you have a molybdenum on the surface and if you increase the acid concentration that is not going to corrode. Why? Because molybdenum as a negative reaction order, negative reaction rate order and so this is considered as the other kind of factors.

The other people called as molybdenum is a getter for chlorides. It can complex into the chlorides; chlorides are the species which promote corrosion. In the pit you have more chlorides and the molybdenum forms a complex into the chlorides and then so what happens? The free chlorides are very less and so, pitting is decreased.

There are also other theories talk about semiconducting theories. The passive film is considered as a semiconductor right? Like high temperature oxidation, you have oxide film and you consider as either rich in oxygen or less in oxygen non-stoichiometric oxygen there right, then you have either p-type or n-type oxide conductors.

So, similarly you can also consider passive film as a semiconductor and what you do? When you add molybdenum, molybdenum has let us say 6+ valency state, then what happens? It will reduce the cations right. When you are going to add a higher ions in the oxide what will happen to a cation concentration? Cation concentration decreases to make the electroneutrality and so, what happens? Then what happens, lowers passive current and makes it stable.

So, there are several kind of you know theories are available, I have just given only few of them and there are some more theories I think, again for this course we do not have to worry too much about the mechanism and just an outline of the mechanisms are. The nitrogen has a similar role about nitrogen still not clear. Some people say it forms ammonia; that means, it neutralizes, but what happens is we have seen that the active dissolution is decreasing, active dissolution is reduced due to nitrogen in the alloy.

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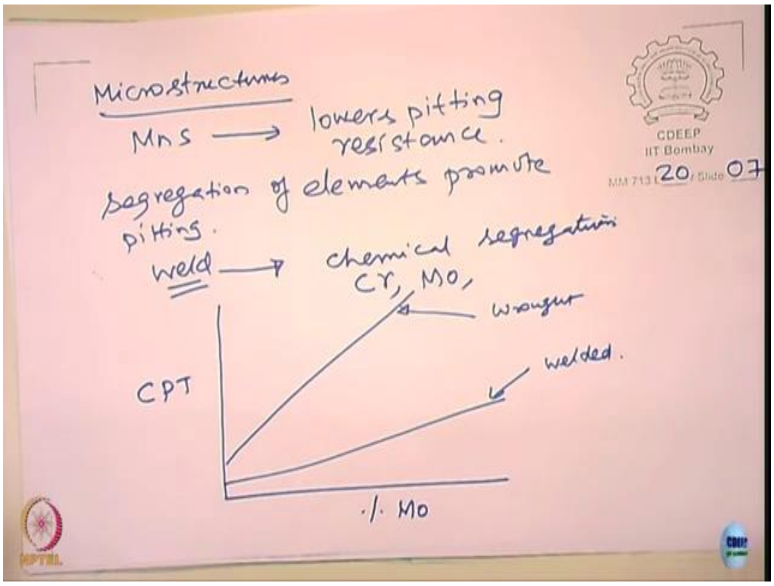

Microstructures

MnS → lowers pitting resistance.

Segregation of elements promote pitting.

weld → chemical segregation
Cr, Mo,

Now, we also have the microstructures. Let us go to microstructures. Suppose you have some phases which are selectively corroding like manganese sulphide, what happens? It lowers pitting resistance they selectively dissolve, attack actually. So, any phase which are prone to corrosion they will promote the corrosion.

Similarly, segregation of elements promote pitting. I give an example: you weld it. If you weld, what happens now? What has happened to the material when you weld it, in the weld fusion zone what happens? Some of you guys are having metallurgy background right, when I weld it by a let us say fusion welding, TIG welding or a MIG welding; you take a stainless steel and weld, what happen? What will happen?

If you look at the microstructure, what do you see the difference between the welded fusion zone and in the base metal? I am talking fusion zone. You take a nicely rolled wrought stainless steel sheet and you weld it and the in the fusion zone what you get? What structure is that? No, have you heard of a cast structure and wrought structure. Have you ever heard of? What kind of structure you will have in a casting suppose you melt and pour it, what structure do you get in the casting?

Student: Dendritic structure.

Dendritic structure see they are very simple, right. See, normally always stainless steel they are all you know melt they have molten liquid pour it and then they do hot rolling and then anneal it out. They make it chemically homogeneous, but when you weld it you are going to have elements which are segregated. Of course, we do not have time to discuss those issues ok.

In the welds you will have chemical segregations like you may have segregation of chromium, molybdenum and things like that. So, you have someplace which is enrich with and chromium, someplace it is depleted with the chromium what will happen to pitting resistance? Pitting resistance will fall because there is some regions are poor in chromium content and moly content.

In fact, if you look at some of the literature published you see, if you see the percentage of molybdenum versus the critical pitting temperature and you see the critical pitting temperature goes like that. It is the wrought and it is welded, what happens? Welded, I will tell you later what is critical pitting temperature.

So, the microstructures play a role because microstructure leads to different chemical variations and so, there are issues of rendering these alloys susceptible to corrosion.

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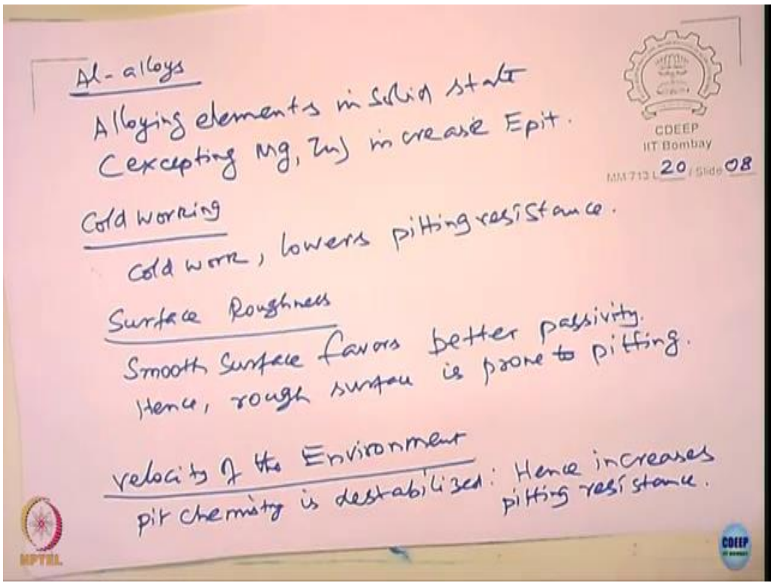

Al-alloys

Alloying elements in solid state

(excepting Mg, Zn) increase E_{pit}.

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Cold working

Cold work, lowers pitting resistance.

Surface Roughness

Smooth surface favors better passivity.

Hence, rough surface is prone to pitting.

velocity of the Environment

pit chemistry is destabilized: Hence increases pitting resistance.

The other example is let us say I just give small example- aluminium alloys. In fact, it is very nice system to discuss and you know how the pitting resistance of the aluminium alloys really change. The aluminium unlike stainless steel will have multiple phases to have the strength.

In aluminium alloys, alloying elements are in solid state, that is excepting magnesium and zinc increase E pit. So, they are generally good, but then you do not make aluminium alloys generally with the elements in the solid solution. You always want to have precipitates to improve the increase the strength performance actually.

But, from scientific point of view can add so many elements like molybdenum, tungsten, chromium and host of elements if you can put them in the solid solution and you will find let us say very significant improvement in the pitting resistance of these alloys actually.

Let us look at the other one metallurgy cold working. Generally cold working and cold work what happens, lowers resistance. Why it introduce a dislocations and so, there will be more corrosion. Surface roughness- smooth surface favours better passivity. Hence rough surface is prone to pitting. So, you make the surface so, do electropolishing you know make it mirror like we will have excellent resistance to pitting at all actually.

The one of the external factor, this not related to metallurgy. External factor like velocity of the environment. So, what do you think will happen to pitting corrosion? You have a stagnant condition; you have flow condition what will happen to pitting corrosion? Pitting resistance will?

Student: Increase.

Increase ok. So, it increases. Why does it increase because it will destabilize the pit chemistry. Hence increases pitting resistance. So, we have seen over all the factors that are controlling the pitting corrosion.

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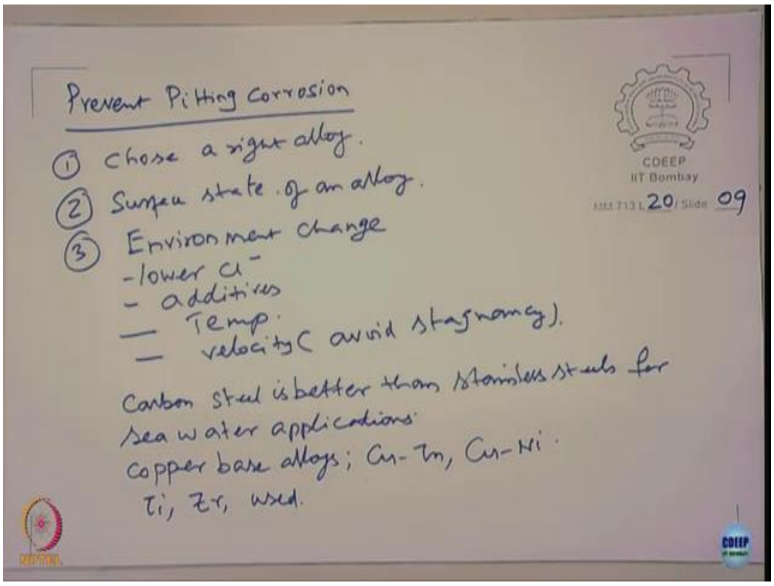

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Prevent Pitting Corrosion

① Chose a right alloy.
② Surface state of an alloy.
③ Environment change
- lower Cl^-
- additives
- Temp.
- velocity (avoid stagnancy).

Carbon steel is better than stainless steels for sea water applications.
copper base alloys; Cu-Zn, Cu-Ni.
Ti, Zr, used.

Then it must be easy for you to say the methods to prevent pitting corrosion. How do I avoid the pitting corrosion? Quickly, yeah. So, you can choose an alloy, choose a right alloy or what you can do?

Yeah, you can change the surface state, to some extent it is not going to be for long run, but yes it is good.

3rd, environment change were possible. If you are going to apply a material for seawater application; obviously, you have to choose the right alloy. You cannot really do much about it right, but if you are talking about a cooling water system or boiler water systems you can change the environment. We can lower chlorides you can do that. Add additives, the temperatures then what happen? Velocity; that means, avoid stagnancy.

If you are going to talk about sea water application the very robust alloy system is what? Titanium right. Titanium forms a very strong passive film and so, it is more resistance to pitting corrosion you have of course, tantalum the ultimate in terms of corrosion resistance and pitting resistance.

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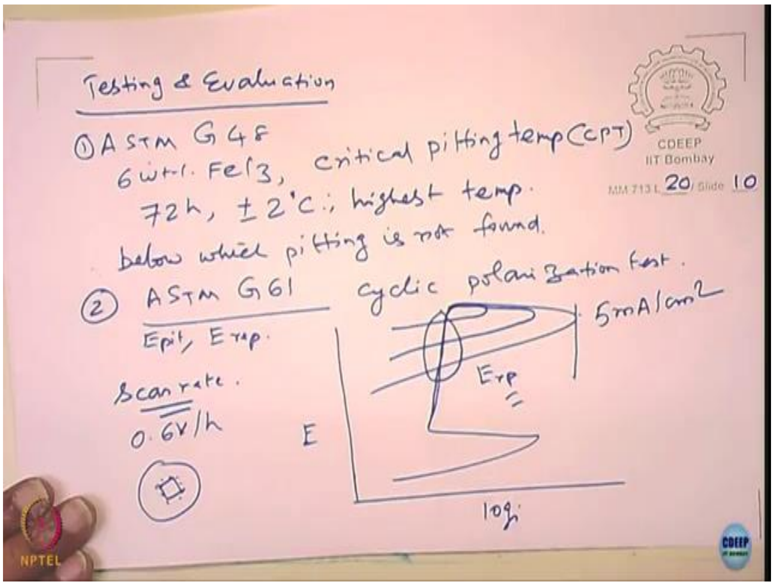

Testing & Evaluation

① ASTM G48
6 wt.% FeCl3, critical pitting temp (CPT)
72h, ± 2°C ; highest temp.
below which pitting is not found.

② ASTM G61 cyclic polarization test.
Epit, Erp.

Scan rate.
0.6V/h

So, let us go to the last topic of this which is testing and evaluation. There are ASTM standards for that you can look at the ASTM standards and ASTM G48 and this talks about the 6 wt. % ferric chloride solution. It determines the critical pitting temperatures. Critical pitting temperature is determined. What you do in this case is that.

You immerse it for about 72 hours, maintain the temperature plus or minus 2 degree accurate, and find out the highest temperature below which no pitting occurs. The highest temperature below which no pitting occurs that is called critical pitting temperatures. Pitting is not found, second one is also we have ASTM G61 it is cyclic polarization. What you do here? You determine E pit, you determine the E repassivation potentials essentially.

See, I am not going to give you all these details you can read this in the standard, is available in the library. I will tell you what is important here. One is this scan rate. Higher the scan rate you get higher the E pit values. So, you have to maintain this scan rate as stated in the standard 0.6 V h^{-1}. There are some problems in order to encounter if you do 0.6 V h^{-1} sometimes you will get a crevice attack in the samples.

Sometimes samples are mounted, you have a mount here you keep the sample and you may get a crevice attack. You must ensure that there is no crevice attack taking place. If there is a crevice attack, then E pit will be lower than the actual value. Why? Before pit occurs the attack takes place along the interface here.

So, mounting the sample properly ensuring that there no attack occurs with the interface between the sample and the mount is a very important thing. In our lab we apply a small bit of epoxy resin and so that the interface is protected from that.

There are also special electrochemical cells available, I think we will not discuss here. You can see them in the literature actually. What is more important is that this reversible current what you talk about here is 5 mA cm^{-2}. Now, if this is not maintained the reversible cell for example, if I just scan like that and I just reverse it here you get like this. If I on the other hand reduce this current even more I get like this.

So, this repassivation potential Erp or Ep whatever you write. Here Erp depends not just on the material it depends upon at what current density you are reversing the scan. I hope you will be able to understand why does it takes place? If you apply more current the pit becomes deeper, it becomes difficult to repassivate if the current is low and the pit is shallow, it is easy to repassivate.

So, repassivation of the pit does not depend only on the metal, but also depends upon the depth of the pit, but what they have found here is if you are going to apply 5 mA and above, it is not going to depend upon this current. So, the in fact, you know it was done work was done in southwest research institute by Narasi Sridhar and group, where they have shown that if you have a critical pit depth beyond which it is not going to affect the repassivation potential.

So, that means, you need to follow this standard meticulously without which you may get a different Ep or Erp value which is not a indication of the pitting growth resistance tendency of the metal actually. Please look at this, it talks about pitting initiation; this talks about the pitting repassivation here. Now, look at this is called initiation now right. When you do this I think we discussed earlier in the class we discussed this one or not?

No, ok. So, then I will spend a minute on this to this discuss what it is, so that you will understand it better.

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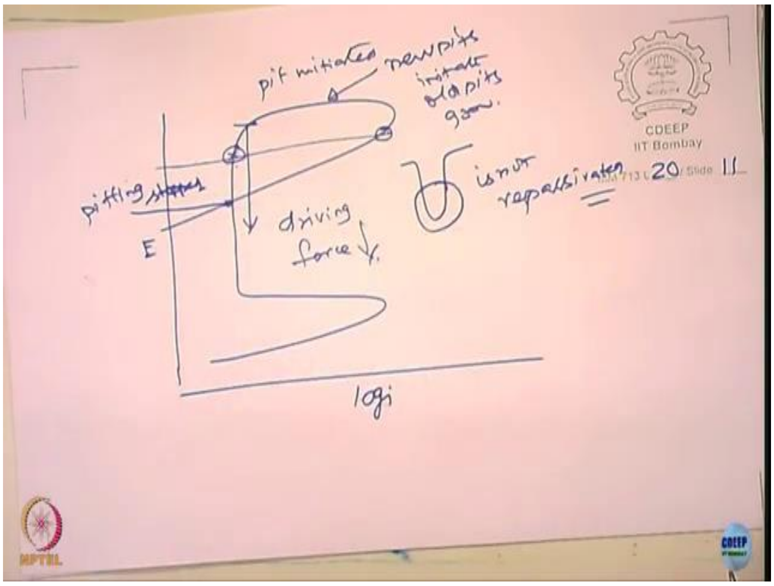

See here you say the pit has initiated. When you advance the potential more and more, what happens here new pits initiate and old pits grow, is it not? So, here the pit will form, it becomes a stable pit here. So, beyond this what happens you know the pit that is formed here is stable, but when you start increasing the current further which means you are going to increase the potential also. Now, what happens the new pits are going to form the old pits grow.

Now, what is happening when you reverse this current here, please see this it is not following the same path rather what happens now, the reverse current is higher than the forward current, right.

Why does it happen? It happens because when you have a pit formed here, this pit is not repassivated. The pit continues to corrode. Even though you are bringing the potential below the E pit, the pit continuous to grow because the pit is now seeing a higher chloride ions and it is seeing a higher amount of H^+ ions and the film is totally damaged, it is not healing at all.

So, when you bring down the potential from here to this, so, what is happening now? The driving force is now decreasing. The overvoltage for the metal to dissolve is decreasing here. So, now, what happens the dissolution current keeps decreasing here, at this particular point of time you can say pitting stopped. The walls become passive now ok; so, that is what really happens now.

So, that is why this is called as a repassivation potential now. So, we will look at the two types of testing for pitting. One is a ASTM G 48 wherein use ferric chloride and determine the critical pitting temperatures and also we also used that particular test to quantify the pitting on a scales. If you go through this standard the standard gives you lot of view graphs to quantify the scales based on the number or based on the depth, based on the radius of that.

We also looked at the electrochemical test where we use cyclic polarization to determine the pitting potential and the repassivation potentials. These two are the important criteria in ranking stainless steel or any material against pitting corrosion in a given environment. Please again notice that the E pit or E repassivation potential also depends upon the environment. It not just only depend upon the material.

So, these two techniques or you know very widely used. Obviously, you cannot use weight loss measurements to determine the pitting because the apparent weight loss is so insignificant it does not give you any meaningful information about the pitting tendency of any alloys. The other important character of pitting corrosion is it is stochastic.

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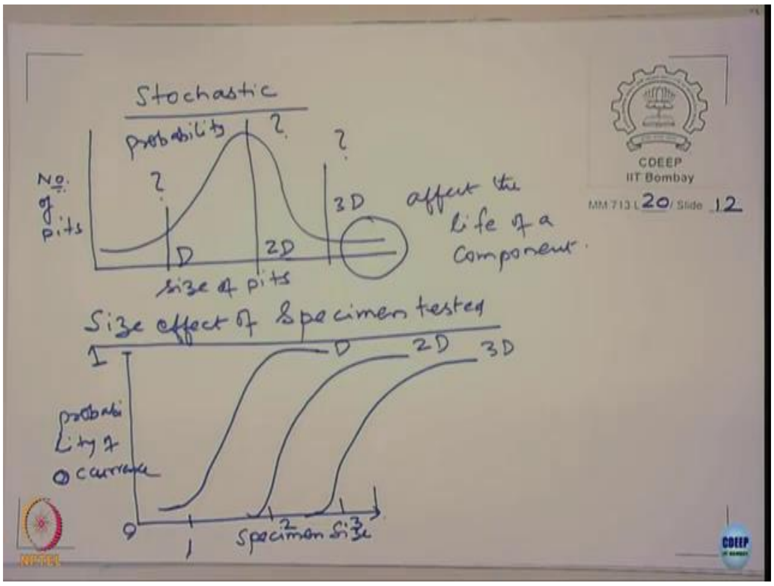

You know what is meant by stochastic, it is more probabilistic in natures. So, that makes some kind of constraint in extrapolating any of the experimental data. So, this aspect we will discuss now.

Now, if you expose a stainless steel or aluminium alloy or any of the alloys which are prone to pitting to a given environment for a given time then you observe the pits that are formed on the surface. You look at the size distribution; you look at the numbers right, the two types of quantification that you can make. So, you can look at the number of pits in a given size and see how it varies. You would probably get a something like this.

The number of pits against the size of the pits you see a kind of normal distribution something like this you will see. What does it really indicate? If you count the number of pits on the lower size and in the highest size both size are very small in number, right. The average size of pits are large in number, but if you talk about a component failure right, what does it depend upon? Suppose, you have pipeline and it has suffered pitting and the leak occurs, the first leak that occur does it depend upon the number of pits, what happen, what does it depend upon?

Student: Size.

It depends upon the deepest pit. So, in practice this is what is going to count for us. This is what is going to affect life of a component. This looks little more even more simple right. Let us look at the size effect of the specimen tested.

Does it really play a role? Now, in order to look at it we take this as a probability concept here. The probability of occurrence of one size of the pit. For example, what is the probability of this pit occurring, what is the probability? We can also look at the probability of this one right.

So, I can determine what are the probabilities of occurrence of a given size of the pit, I can do that right. If I can expose the samples of various sizes and determine the probability of occurrence of any of these size pits, I assume let us say this is the size of the pit, let us say D is the size of the pit, let us say 2D is size of the pit and 3D is the size of the pit right I have given approximately.

And, if I plot the probability against specimen size probability of occurrence or the pits, this say a 0 and you say 1 probability right. And, I for simplicity I also write the size in terms of unit sizes. Let us say the size of the specimen is 1 unit area, 2 unit area, 3 and 4 like that I can have right. Unit 1, this is the 2, 3 and maybe you can say 4 up to let us go up to 3 only.

So, what I mean by that suppose I take this is 1 cm^2, this is 2 cm^2, 3 cm^2. Let me look at the probability of finding the pit of diameter D that is here. The very interesting that the property of finding the pit D in the sample one like that goes like that. So, the size of this pit the probability of finding that size of the pit increases when the size of the sample.

Student: Increases.

Increases. Now, you can also find out similar thing for the pit size of 2D. So, what do you understand from this particular plots?

Student: If the size is increasing, the probability of finding deeper pits is more.

More. So, it means if the structure is more in reality, if you are going to go for larger structures, the probability of pitting is going to be larger; the smaller structure, the probability of pitting becomes less. So, it is a stochastic process. So, in a laboratory suppose you take a very small size of a sample and somebody takes a larger size sample it is possible that you may get different results, not necessarily you get the same kind of results actually. So, this makes the things more complicated.

There are several reasons one can attribute to that. Suppose, I take a stainless steel, the stainless consists of what consists of inclusions right the probability of finding an inclusion which affects the pitting is more when the size of the sample is larger. So, this is the one aspect of thing and people have in fact, dealt with this see the probabilistic theory of pitting corrosion you know has been one of the important topic of research.

We will not go more detail into it, the idea is to expose to you the complexities involved in determining the pitting tendency of a samples. So, that is why when you do test especially corrosion test you give all information size of the samples, environment, the duration, temperatures these are all their several factors that affect the corrosion behavior of the metal. So, in this case the size becomes even more important and relevant for us to consider actually. So, that is something you should you should look at it.

So, and one thing I just forgot to mention about the prevention of pitting corrosion I think if you can go back to this slide some time back we discussed actually ok. Please recall this discussion I just going to add, we said that the pitting corrosion can be prevented by of course; choosing a right alloy of course, this is a very generic way of talking about it.

And, it also can you need to look at the surface state of the material how polished, the environmental changes- chloride should be reduced, you can add additives, you can lower the temperatures and you avoid stagnancy and all. But of course, the material selection depends upon what? Depends upon a given environment right, the temperature, the chlorides, the pH conditions and so, you decide what can be the alloy that is suitable for that.

And, for that you also have test like critical pitting temperatures, E pit values. Please again notice; these are all ranking of the materials. I do not think that these tests are going to give you any kind of life that you can supposedly you know you can predict that is simply not possible so far about the pitting corrosion or the metals.

Coming back to this the first aspect that is the choice of alloy and when it comes to stainless you know that, right? You know that you want to increase the pitting resistance the one way to look at is that composition which is pitting resistance equivalent number. It goes high then I think the pitting resistance increases.

But, the other way of looking at is you choose an alloy which is not passivating. For example, carbon steel is better than stainless steels for seawater applications. That is why ship hull is made up of what? Made up of carbon steels not the stainless steel.

But, what is the problem with the carbon steels? The uniform corrosion rate is more. The uniform corrosion rate is more than that of the stainless steels, but you have the problem about uniform corrosion then you go for copper base alloys. What are the alloys that you can think of? You can think of brass, you can think of cupronickel alloys. They are all was used in sea water applications. They have reasonably good uniform corrosion resistance compared to carbon steels and they do not pit and so, they are in fact, widely used for seawater application.

The other way of looking at it is you have a very strong passivating metals and alloys, very strong passivating that is we saw PREN number. Similarly, you can look at titanium, zirconium these all can be used. Titanium is used actually for sea water application, it’s strong oxide films are formed at ambient temperatures. Slightly elevated temperatures titanium can be very well used. So, to summarize pitting corrosion a pitting corrosion occurs predominantly in the?

Student: Passive metals.

Passive metals, all right?

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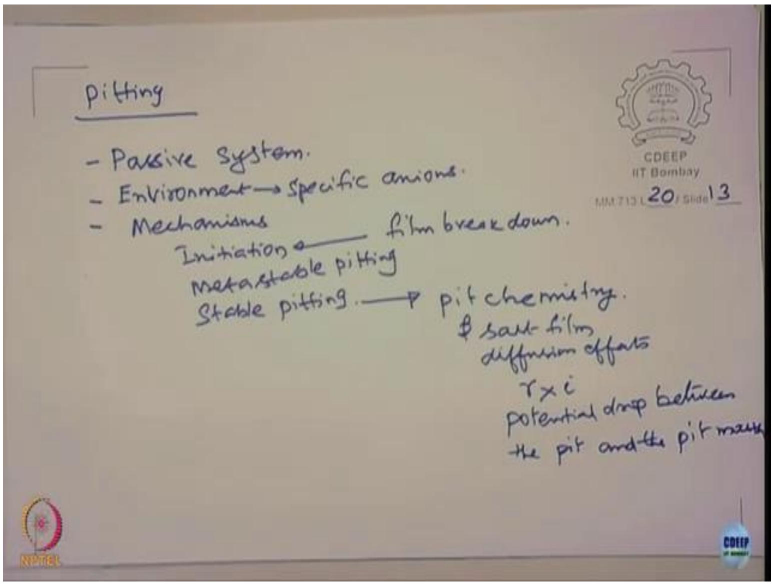

pitting

- Passive system.
- Environment → Specific anions.
- Mechanisms
  - Initiation ← film break down.
  - Metastable pitting
  - Stable pitting. → pit chemistry.
    - & salt film
    - diffusion effects
    - $r \times i$
    - potential drop between the pit and the pit ma

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Only the pitting I put it as passive system. You know there are metals like titanium, stainless steels. Titanium are all passive in a wide variety of environments. But, we also know that you can also passivate many metals depending upon the environment you make it, pH slightly favourable. Even steel can do, magnesium can undergo passivation and in such cases they can undergo pitting.

So, it is the passive system, it also depends upon the environment, specific anions I specially put it. Of course, cations also can influence right can cations influence pitting corrosion? Yeah?

Student: Cation accumulation.

Of course, that is there. Another part of it I am talking about the environment; I am not talking about the cations dissolved in the pit and a causing the pH change ok, I am talking about external addition of cations.

Student: If they are oxidizing agents.

Yeah, oxidizing agents right- ferric ions, cupric ions, mercury chloride all the highly oxidizing environments can cause pitting environment of course. But, then anions are very important. We talked about the pitting mechanisms. We looked at especially what initiation, then we talked about metastable pitting then we talk about stable pitting right. The initiation is governed by what? Film breakdown am I right? film start breaking down because of the anions present in the environment.

Initiation mechanisms still are not well defined, still not 100 percent clarity is there. I have looked at the metastable pitting right when the film breakdown takes place, there is a localized damage micron or sub micron levels and how do you know it is metal undergoes metastable pitting? If you look at the current oscillations if you are going to apply a potential in the passive region over the sample and you monitor the current, there is no stable current, there is always a fluctuation in the current right.

And, as you move the potential towards the pitting potentials the fluctuation increases. These fluctuations indicate that there is a breakdown of the film and then there is again healing of the surface by reforming the film. And, the criteria of a metastable pitting turning into a stable pitting right, what is the criteria for this? When does it becomes stable? Yeah, when does it become a stable pit?

Student: Pit chemistry.

Yeah, it is a pit chemistry, right. It is the pit chemistry. The pit chemistry is special, it has got more H^+, it has got more chloride. So, it does not allow the metal is to repassivate. So, that is governed by what? Salt film, diffusion effects, we also had a criteria called as r-i criteria we talked about, right. It also depends upon the potential drop; drop between what? Between the pit and the pit mouth because there is a potential drop it does not allow the pit it is a growing pit the different will allowed to repassivate right. They are all kept at a more negative potential, that is why it occurs. We talked about the mechanisms.

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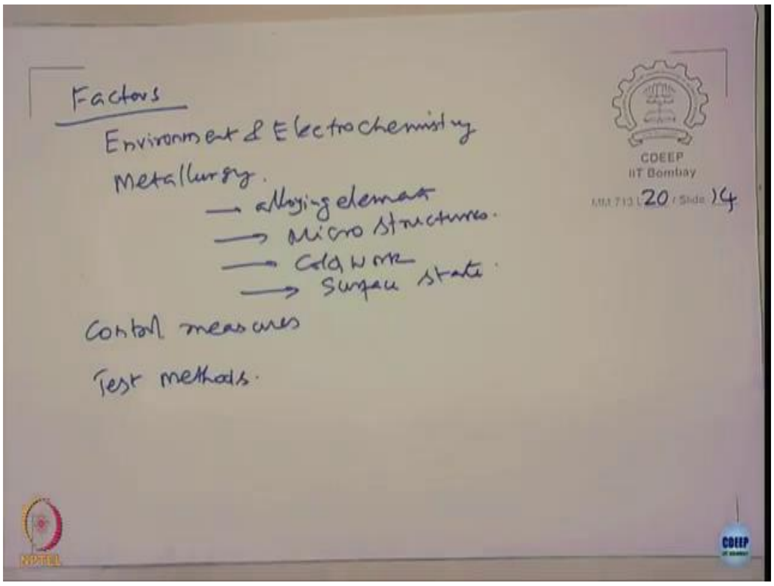

Factors

Environment & Electrochemistry

Metallurgy.

- alloying element
- Micro structures.
- Cold work
- Surface state.

Control measures

Test methods.

Then we talked about the factors controlling the pitting corrosion. This is environment and electrochemistry, metallurgy, right. We looked at the temperatures, we looked at the pH, and we look at the velocity effect for example. You have a very greater influence on that.

The electrochemistry means what? It is the potential. If you are going to move the specimen towards pitting potential it is going to break film is going to break and you are going to have a higher damage to the passive films.

We also look at the metallurgy in term mostly we have seen in relation to stainless steels and how the various alloying elements affect the two parameters pitting potential and the repassivation potentials.

We saw that various alloying elements. Microstructures, they do significantly affect pitting corrosion. When I say microstructures it could be all kind of things; it can be segregation of various phases and we talked about cold work right. I forgot to summarize and we also defined what a pitting factor is.

This is just not that an uneven corrosion, it can be defined as a pitting. The radius of the pit to the depth of the pit is very important. You should have the radius would be smaller compared to the depth of the pit, then only the pit can be stable. Then we look at what?

Looked at the control measures, and we looked at the test methods. Of course, you can add one more to this and metallurgy, the surface state.

Any questions in pitting corrosion so far? Ok. There are no questions, we will shall close the discussion on this topic of pitting corrosion.