Corrosion Failures and Analysis
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Lecture - 32
Pitting Corrosion: Mechanism and Protection

Let us start lecture 32 the course is Corrosion Failures and Analysis, and we will conclude Pitting Corrosion today, we will look at the mechanism of pitting and then also try to see some of the protection procedures or routes one can employ to avoid pits.

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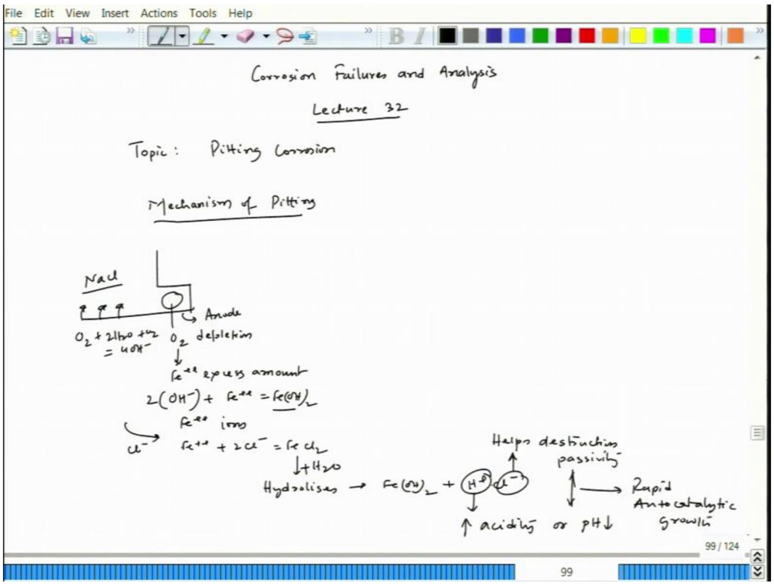

Corrosion Failures and Analysis

Lecture 32

Topic: Pitting Corrosion

Mechanism of Pitting

NaCl

Anode

$O_2 + 2H_2O + 4e^- = 4OH^-$

O_2 depletion

$\downarrow$

Fe^{++} excess amount

$2(OH^-) + Fe^{++} = Fe(OH)_2$

Fe^{++} ions

Cl^-

$Fe^{++} + 2Cl^- = FeCl_2$

$\downarrow + H_2O$

Hydrolises → $Fe(OH)_2 + H^+ Cl^-$

Helps destruction passivity

↑ acidity or pH↓

Rapid Autocatalytic Growth

Now, the course is failures and analysis corrosion failures and analysis lecture 32 pitting corrosion we will look at mechanism part. Now, as we see that in case of crevice, we could see that we have a crevice and within this crevice we have oxygen depletion that lead to finally, after having excess Fe plus plus generation because this portion will be anode and Fe plus plus excess amount.

Since the OH minus whatever is available that would react with Fe plus plus 2 equal to Fe OH whole 2, but since we have huge amount of oxygen reduction in NaCl solution, it has to produce more Fe plus plus ions and that would be excess once the solubility product of this particular species exceeds.

So, then only Fe plus plus will be extra in the solution in the within this crevice and then chloride ion comes in it reacts with Fe plus plus just to neutralize that excess positive charge within that crevice and this one then hydrolyzes to generate hydrolyzes and generate FeOH plus H plus chlorine minus H_2O react with H_2O.

Now, here we generate H plus and chlorine minus. So, H plus ion increases the acidity or ph decreases and this chlorine ion helps destroying destruction of passivity. So, both of them then lead to rapid auto catalytic growth of auto catalytic growth of crevice corrosion part, ok.

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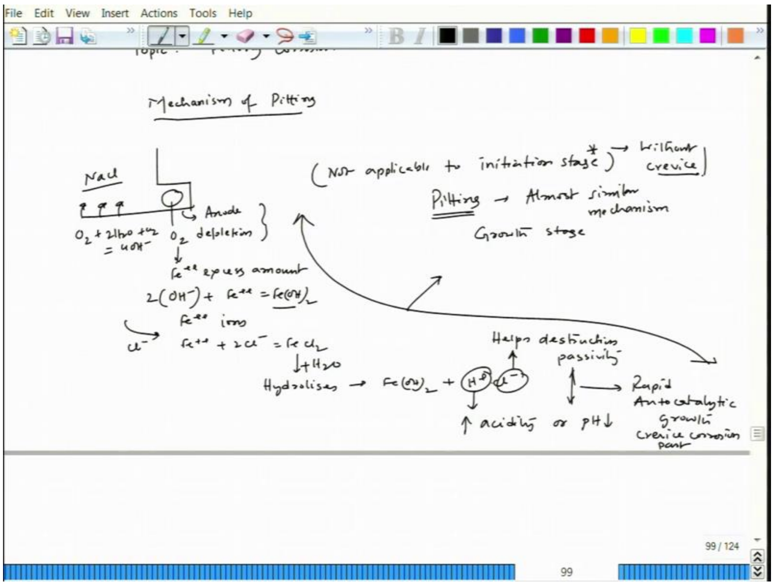

So, that is the mechanism what we have seen in case of crevice. Interestingly, the mechanism part of pitting becomes exactly same; this particular entire part for pitting it holds almost similar mechanism.

Now, the only difference is, so, if you consider that this part depletion of oxygen, this happens and the entire thing happens during the growth stage. So, this entire thing whatever the mechanisms mechanism we have just indicated in case of crevice, it is the basically growth stage mechanism in case of pitting, but this is not the initiation stage. This is not applicable to initiation stage.

Now, why we say this initiation stage because for crevice we know that we have a we have a design part of that particular crevice; that means, the crevice section is wide enough to allow electrolyte ingress and it is narrow enough to maintain stagnant condition, ok.

Now, in case of pitting, pitting can happen even without having crevice one can have pitting. For example, if you had if you could recall the plate what we have shown that stainless steel plate with a lot of perforated pits. So, that plate was flat without having any crevice, but still it had pitting. So, pitting can happen. So, this initiation part, this part can happen even without having without crevice.

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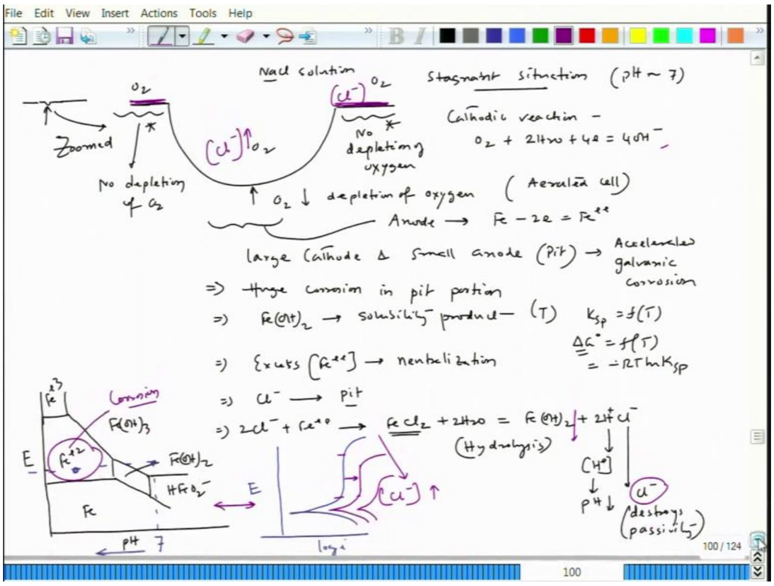

Stagnant situation (pH ~ 7)

Cathodic reaction –

$O_2 + 2H_2O + 4e = 4OH^-$

(Aerated cell)

Anode $\rightarrow$ $Fe - 2e = Fe^{++}$

large Cathode & Small anode (Pit) $\rightarrow$ Accelerated galvanic corrosion

$\Rightarrow$ Huge corrosion in pit portion

$\Rightarrow$ $Fe(OH)_2 \rightarrow$ solubility product – (T) $K_{sp} = f(T)$

$\Delta G^\circ = f(T) = -RT \ln K_{sp}$

$\Rightarrow$ Excess $[Fe^{++}] \rightarrow$ neutralization

$\Rightarrow$ $Cl^- \longrightarrow$ pit

$\Rightarrow$ $2Cl^- + Fe^{++} \longrightarrow FeCl_2 + 2H_2O = Fe(OH)_2 \downarrow + 2H^+Cl^-$

(Hydrolysis)

$[H^+]$ $\downarrow$ pH $\downarrow$

Cl^- (destroys passivity)

Now, let us see what happens during the growth stage. Let us say first of all let us not get into this initiation stage let us say some pit has initiated this is a pit let us say a small pit this is a small pit and this one we have zoomed and we are seeing this. Now, within this small segment and if it is a stagnant situation, then initially everywhere we had let us say oxygen content same.

Now, since this and let us say this is NaCl solution. So, that means, aerated NaCl solution so, that means, the ph is you can say 7, so, that means, a neutral solution. So, the cathodic reaction would be 4 OH minus. So, this particular cathodic reaction so, it happens everywhere.

Now, after some time because it is a stagnant solution, the oxygen content within this pit here so, the oxygen content drops down. So, that means, it is a depletion of oxygen.

Now, this particular portion no depletion of oxygen. Here also, no depletion of oxygen fine. So, that means, if it is depleted and the other section the flat part of it is not depleted with oxygen this cathodic reaction will continue to happen in this section as well as in this section, but since it is depleted oxygen so, it is a aerated cell and the pitting part this pitting part would become anode.

So, now because it becomes anode anodic reaction would take place there. Now, since if you consider this small pit which has been zoomed here now in a small segment we have Fe plus 2 and the rest of the part we have huge area. So, again it actually having a situation of galvanic corrosion where cathode area where large cathode and small in fact, this becomes tiny anode pit portion and this is a typical accelerated galvanic corrosion.

So, this is the condition for accelerated galvanic corrosion. So, this portion the pit portion it would lead to huge dissolution of in pit portion. So, that means, again it will have Fe OH whole 2 formation and it is have having its own solubility product and that is a the function of temperature because solubility product Ksp is basically function of temperature of y because delta G is a function of temperature and this is basically minus RT ln K_{SP}.

$$K_{sp} = f(T)$$

$$\Delta G^o = f(T)$$

$$\Delta G^o = -RTlnK_{sp}$$

So, this is related to the free energy. So, that is what it becomes temperature function and pressure is constant. So, in the solubility product if it exceeds in that particular section, so, that means, the rest of the iron ion will start coming up extra ok. So, now it is excess Fe plus plus ion and this needs neutralization because within this small segment we have a excess positive charge. So, that excess positive charge chloride ion will move to will migrate to pit portion.

Now, this chloride ion will react with Fe plus 2 and it forms $FeCl_2$ and this $FeCl_2$ since there are water molecules it will hydrolyzes. This particular part it becomes FeOH whole 2 plus HCl, ok. So, plus minus and since it is a strong acid that is what I have written in terms of plus and minus those ion forms this process is called hydrolyzation hydrolysis.

So, this hydrolysis would lead to excess hydrogen ion which would lead to reduction of ph becomes it becomes more acidic and excess chlorine ion which disturbs or destroys passivity fine since there is a excess chlorine ion. Now, this destruction of passivity means a lot in case of pitting corrosion.

pH of course, we know that with the increase in pH if we try to see a Pourbaix diagram E versus pH the plot of iron probe diagram is sort of like this. Now, where this part is so, this is pH this part is Fe which is immunity zone Fe plus 2, this is Fe plus 3, this is Fe OH whole 3, this is FeOH whole 2, this is H Fe O 2 minus.

Now, in this case as you see if the potential is maintained here let us say the potential is here and the pH is let us say 7. So, that means, it is in a passivating condition. Now, if the pH drops down because of the increase in hydrogen ion concentration, so, if it comes here, so, that means, it is ending up in the corrosion zone. So, that enhances corrosion.

Now, chloride ion we have seen that if we try to look at the breakdown potential due to chloride presence E versus log I we have seen that let us say if it is a cell passivating ok. So, that means, that case the curve will move like this. This will move up, this point will move up and this point this particular thing will move towards right and this particular potential also drops down as the chloride ion concentration increases. So, like that way so that means, this way chlorine ion concentration goes up.

So, that kind of situation we had already seen. So, the chloride ion excess chloride ion would actually destroy the passivity within the pitting. So, the pit would not repassivate because of the even there is a chance of repassivation chloride ion will not allow that pit portion to repassivate.

So, that allowed to pit to grow at a enormous pit because it has to maintain electro neutrality, for that chlorine ion has to come to neutralize that excess positive charge and excess positive charge is forming because you have to supply electron for this cathodic reaction happening over the entire flat surface and that chloride ion will lead to ion chloride formation, hydrolysis and then acid formation and this one settles down ok because this is again hydroxide.

So, that means, we do not have any passivating situation we have corrosion situation because this is reaching to a corrosion section this is basically corrosion section in probe diagram. So, that means, there is a there is a kind of interlinking between kinetics and thermodynamics. So, this probe diagram is thermodynamic part and this E versus log I plot is basically kinetic part. So, that are interlinking and then it is leading to excessive dissolution or auto catalytic dissolution within the pit portion.

Now, interesting part is let us understand chloride ion concentration little more. Now, here chloride ion concentration is very high and here chloride ion concentration is not that very high, ok. So, now, if it is having a passive layer passive layer that passive layer would not get disturbed ok during the growth stage because the chloride ion concentration within the pit has gone up. So, it will not allow the pit to repassivate, but the other portion the flat portion other than the pit region will have passivity and that will provide the surface for cathodic reaction.

Interesting situation here that the chloride ion is not allowing the passivity to achieve within the pit, but it will allow it will not it because the concentration of chloride is not that high on the flat surface the passivity will maintain and this also indicates that the growth of pit is actually protecting the other surfaces.

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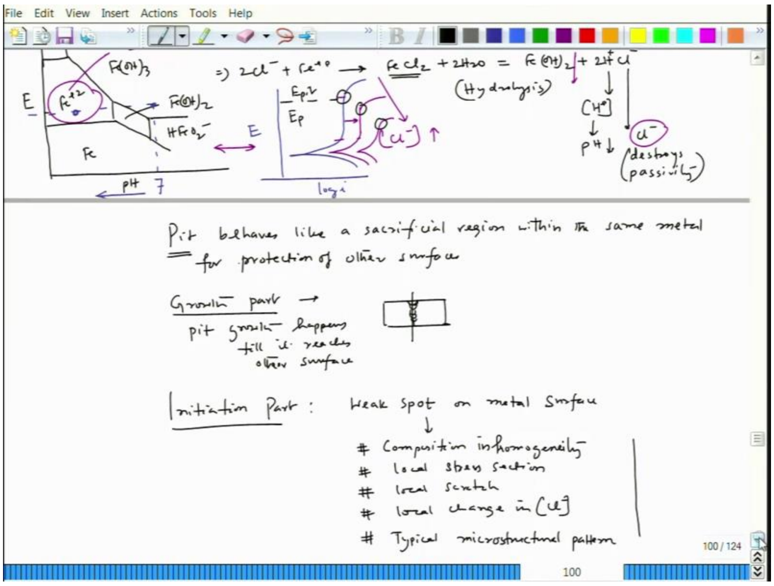

$\Rightarrow 2Cl^- + Fe^{+2} \rightarrow FeCl_2 + 2H_2O = Fe(OH)_2 + 2H^+Cl^-$

(Hydrolysis)

$[H^+]$ ↓ pH ↓

Cl^- (destroys passivity)

Pit behaves like a sacrificial region within the same metal for protection of other surface

Growth part →

pit growth happens till it reaches other surface

Initiation Part : Weak spot on metal surface

↓

Composition inhomogeneity
local stress section
local scratch
local change in $[Cl^-]$
Typical microstructural pattern

So, actually pit is acting like a sacrificial portion so, the pit behaves like a sacrificial region within the same metal for protection of other surfaces of the same metal. So, that means, here sacrificial for sacrificial activity we do not need another metal. So, the pit itself is acting like a sacrificial anode region which protects the other surfaces.

Now, interesting part is that happens because of this phenomena. This phenomena is exactly same as what we have shown in case of crevice, but pitting cannot be considered crevice because pit can happen on the flat surface also. It does not need that crevice to achieve crevice to crevice to form and then crevice corrosion starts it happens anywhere on the on a metal surface without having any crevice.

Now, interesting part is initiation. So, this is the growth part. So, whatever I said this is the growth part and this growth would stop when the thickness it goes through thickness. So, that means, if we have a metal cross-section so, let us say here the pit happens. So, the pit grows like this and then finally, leak happens. So, that is then the growth stops. So, till then pit grows till it reaches other surface, right. So, this is a typical nature of pit even crevice case also crevice stops when the entire metal sub section is perforated.

Now, coming to the initiation part, so, as we have indicated before that initiation can happen on a weak spot weak spot on metal surface.

So, that weak spot could be compositional inhomogeneity, it could be due to local stress section, it could be due to local scratch, it could be due to local change in chloride ion concentration at some location if the chloride ion concentration suddenly goes up then definitely that can happen, it could be due to inhomogeneous or you could we could be due to typical microstructural pattern microstructural pattern – we have all explained these things before. So, there pit can start and the growth stage of course, the way it happens we have just explained. So, that is basically the mechanism part of it.

Now, when we talk about this pit formation here we check that is there any because it is definitely related to potential because we could see that these are the potential which is called E pit or in short it is called E P. Now, question is whether that is the potential we have to worry or we have to find out some other potential where the pitting will not happen if we do not reach to that potential, ok.

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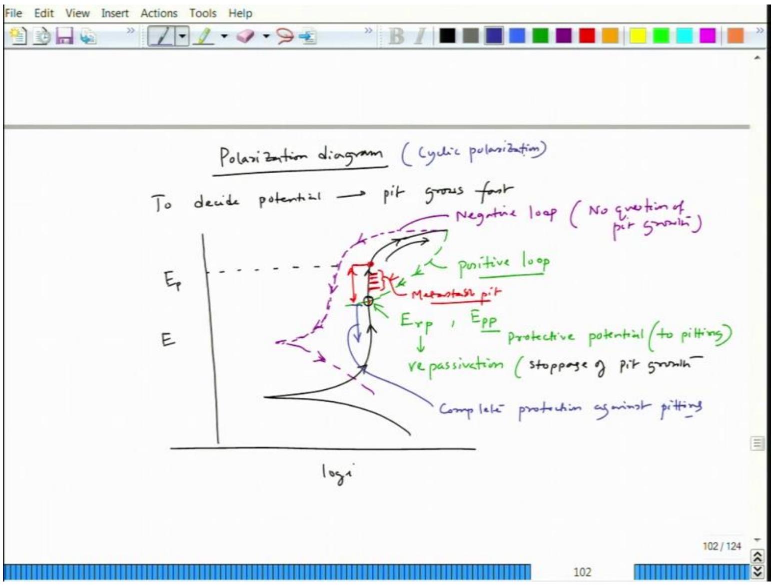

Polarization diagram (Cyclic polarization)

To decide potential → pit grows fast

So, let us see in order to understand that we have to get into we have to see polarization diagram again to decide the potential where pit grows fast. Now, if we see a cell passivating system E log i in that cell passivating system the graph look likes looks like this and here we are seeing that this is my E pit, ok.

Now, if we do cyclic polarization, then let us say it has gone to this level and from that we are reverting back in the potential axis. So, if we revert back, it can come this way and it can have a kind of graph like this which is called negative hysteresis or negative loop. It can also happen, so, this negative loop is happening ok.

Now, if this thing happens we say that there is no question of pit growth, ok. So, there the system is absolutely stable and has a good resistance to pitting. Now, if we have positive loop the positive look loop looks like this, it cuts like this ok. So, when the positive loop cuts like this is called positive loop this is a typical response of a cell passivating system showing pitting aggressive pitting.

Now, the potential where the reverse curve, so, this is the forward reverse curve. So, this is the forward curve and this is the in this case this is the reverse curve which is the negative hysteresis or negative loop and in this case is a positive loop and this is the negative this is the reverse polarization. So, this potential has got a huge importance.

This potential called E rp ok or some book you will find this is called E PP. So, the rp is repassivation and this is PP is protective potential. In fact, protective potential to pitting fine and this is also repassivation; that means, we say that the whatever pits have formed here during the forward movement. So, these pits when it reverses back at this potential it would repassivate again; that means, it will not grow ok. So, that is what this is called repassivation potential. So, this is related to stoppage of pit growth.

Now, if we go this way, so, that means, this is moving like this ok now if we see between this to this we can do sometimes we do experience a kind of small serration in the graph and those serration actually nothing, but metastable pits. So, these are metastable pit.

So, this metastable pits may not grow completely till it reaches E P or pit potential and once it reaches this pit potential, the existing pits they will start growing at a very very high rate. So, then we cannot have any protection, but till metastable phase pit forms it is ok, but they are not growing rapidly.

Now, the best possible way to have a protection is operate operation of that particular metal below this potential below this potential. This particular below this potential we say complete protection against pitting. So, this is interesting. So, this potential needs to be sometimes we need to find out by doing a cyclic polarization this is called cyclic polarization.

So, now, let us not extend our discussion on pitting because if we want that we can have a complete lecture session on pitting corrosion. So, let us get into the some of the protections what we can have from the pitting part, ok.

So, now, if we talk about protection from pitting, so, that protection of pitting in order to have it we can follow different practices and most of the practices would follow just to avoid the conditions which are which are suitable for pitting, ok. So, mostly those are the protections apart from the there are other protection. So, let us understand those protection part.

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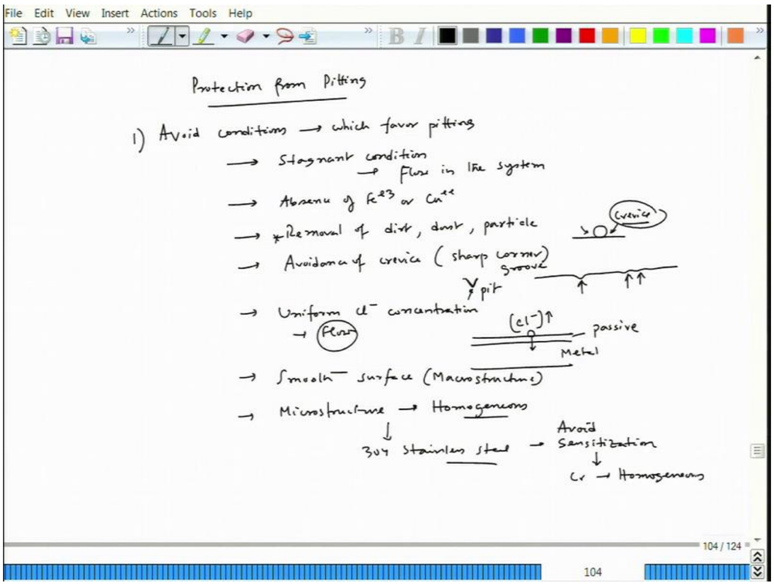

Protection from Pitting

1) Avoid conditions → which favor pitting
- → Stagnant condition
  - → Flow in the system
- → Absence of Fe^{+3} or Cu^{++}
- → *Removal of dirt, dust, particle
- → Avoidance of crevice (sharp corner) groove
  - pit
- → Uniform Cl^- concentration
  - → Flow
- → Smooth surface (Macrostructure)
- → Microstructure → Homogeneous
  - ↓ 304 Stainless steel → Avoid Sensitization
    - ↓ Cr → Homogeneous

So, the protection from pitting. So, now, first foremost is avoid conditions which initiate which favor pitting, what are those? One is stagnant condition. So, better to have a flow in the system and remember when we have a flow in the system that flow should be at a at a not very high flow rate because high flow rate would also create problem that has a problem associated problem with the high flow because that would lead to erosion corrosion.

So, the flow should be such that it does not allow the stagnant condition to maintain. So, this is one. So, then one can have absence of Fe plus 3 or copper plus plus. So, these are the ions which are oxidizers they can also lead to pitting. So, if we do not have them, pitting can be avoided and that can happen that can come within the system within this particular container of metal through the inlet flow, ok.

So, for example, copper ion can come into the iron tank if we have that inlet pipe if we make of make out of copper or brass pipe so then copper iron can get in. So, that can lead to a deposition of copper due to cathodic reaction and then copper deposit would act as a cathode and there pitting can start. So, that if we can avoid that then definitely pitting can be avoided.

Then removal of dirt, dust, particle small particle those are the regions where it can form a small crevice kind of appearance and then and that can initiate pit. For example, if it is a small dust so, this actually crevice. So, there pitting can start. So, now, when we come to this crevice the crevice is initiation of pitting sometimes.

So, this crevice removal of or avoidance of crevice avoidance of crevice how can we do it? By doing this one that removal of dirt dust particle, the regular cleaning and in fact, if we have a flow in the system in that can actually clean off dirt and dust. So, that can lead to bit of erosion corrosion, but since the dirt is actually continuously moving through the stagnant situation would not arrive and that would avoid pitting related pitting related problem which initiate which is initiated due to formation of crevice.

So, the avoidance of cravings crevice; that means, avoid sharp corner sharp corner. So, because for example, if we have this kind of appearance of a particular metal surface the pit can start here, ok. So, for example, a metal surface if it is uneven, so, these are the points where pit can initiate ok. So, that is what the sharp corners or groove better word is groove. So, those grooves are to be avoided.

So, these are and then of course, if we can somehow maintain uniform chloride ion concentration, if it is a flat surface and that locally chloride ion concentration if it goes up that actually disturbs the passivity and that disturbance can lead to a small appearance of pitting.

For example, if this is a let us say the passive layer, this is the metal, this is the passive layer and if the chloride ion concentration momentarily increases here so, the pit starts forming here because that at that location pit will grow aggressively because the rest of the part will be protected due to the anodic sacrificial effect of that pit, ok and that actually initiates due to increase in chloride ion concentration.

So, uniform chloride ion concentration that can only be maintained by a flow. If there is a flow within the system definitely that would maintain a more or less homogeneous chloride ion concentration, ok. Now, these are the kind of conditions for example, other conditions are as we have said that smooth surface rough surface has a higher tendency to form pit if we can maintain smooth surface it is absolutely fine smooth and shiny surface. So, that would not create pit.

Now, a microstructure because if you recall we talked about macro structure and microstructure this comes in macrostructure mode and this is microstructures, more or less if we can maintain homogeneous microstructure homogeneous that would help avoiding pitting.

For example, the best example is stainless steel 304 stainless steel. So, that 304 stainless steel if we avoid sensitization avoid sensitization of course, you can avoid pitting, ok. So, that means, if it is avoidance of sensitization means chromium content becomes homogeneous, fine. So, that avoid that actually would lead to avoidance of pitting.

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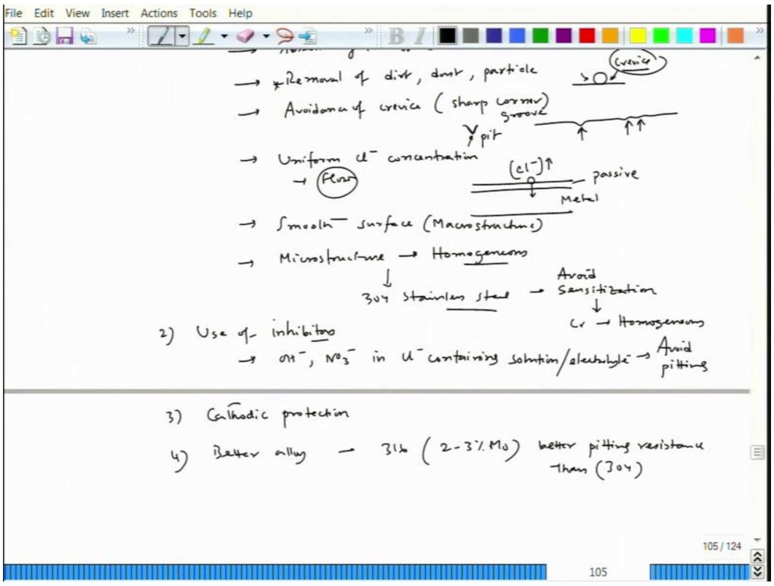

→ Removal of dirt, dust, particle

→ Avoidance of crevice (sharp corner, groove)

→ Uniform Cl^- concentration

→ Flow

$(Cl^-)\uparrow$

→ Smooth surface (Macrostructure)

→ Microstructure → Homogeneous

↓

304 Stainless steel → Avoid Sensitization

↓

Cr → Homogeneous

2) Use of inhibitors

→ OH^-, NO_3^- in Cl^- containing solution/electrolyte → Avoid pitting

3) Cathodic protection

4) Better alloy – 316 (2-3% Mo) better pitting resistance than (304)

So, these are the some of the conditions. Now, second part is of course, use of inhibitors which can avoid pitting, ok. Now, sometimes we do people do use OH minus or nitrate in chloride containing solution or electrolyte and that avoid pitting, fine. Now, some people can use one can use cathodic protection. 4th one can use better alloy for example, 316 which contain around 2 to 3 percent molybdenum is having better protection better pitting resistance than 304 ok.

So, these are the usual routes one can follow to avoid pitting ok. So, let me stop here we will continue our discussion on other form of corrosion. So, the form what we will start in our next lecture is erosion corrosion. So, till then thank you.