Surface Engineering for Corrosion and Wear Resistance Application
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Lecture - 14
Corrosion – III

Hello welcome to the IIIrd part of degradation due to Corrosion talks. So, in this part I will discuss about the details of pitting corrosion specially pitting normal pitting connection as well as cavitation corrosion, intergranular corrosion and selective leaching.

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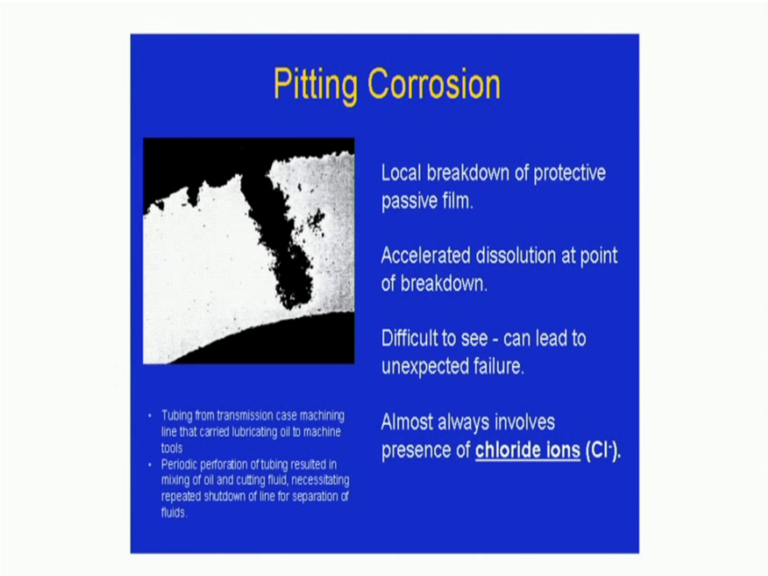

Now, if you talk about pitting corrosion this is also a kind of localized form of corrosion which looks like pitted on the surface. So, after this corrosion you will find that there is pit formation on the surface and the driving for the particular pitting corrosion is nothing, but again local breakdown of the protective passive film and subsequently galvanic cell formation between the expose surface and also the protective surface.

And then subsequently attack of the non protective part and this particularly leads to formation of pits and pit actually proceeds or it propagates towards the direction of the gravity and as gravity. And as a result of which you will find that there is speeds are very large aspect ratio and it is a kind of dangerous form of corrosion because once the pit formation starts it propagates in an autocatalytic fashion and as a result of which within a very short period of time there is actually perforation of the material and which is even not visible.

When you see the pitted surface you will find that the there are pit formation here or there sometimes it is visible sometime it might not be visible because sometimes it is also covered by the corrosion debris and outer part or surrounding area is highly reflective in nature. So, we will find that there is a completely nope no sign note signature of the corrosion in the surrounding region.

So, you might field that there is no corrosion attack on the surface, but actually it is pitted and because of pitting there is perforation of the component to a large extent. So, this is a kind of insidious form of corrosion and this is advocated again and almost most of the cases it is observed when there is chloride spaces in the environment.

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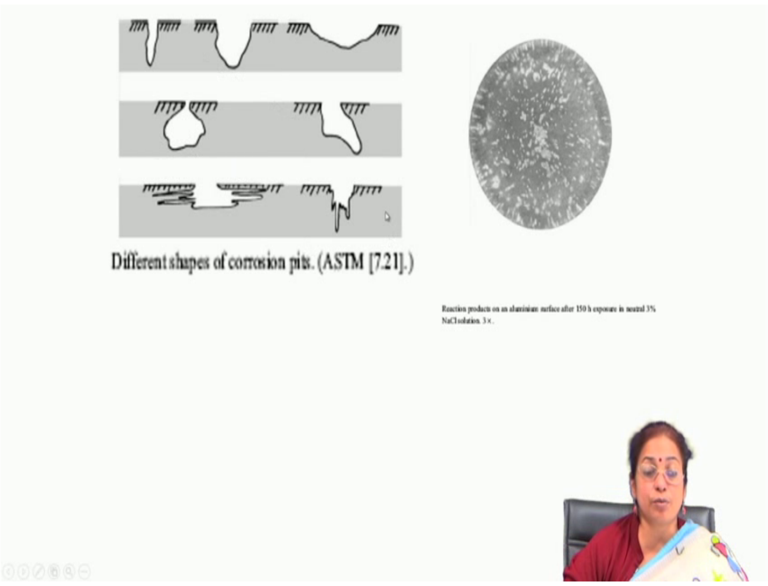

Now, if you quickly go throw the pitted surface on the surface it appears likes small small pits having different dimensions, starting from micrometre starting from nanometer to micrometer to macrometer level. And if you just quickly go through the depth or it how it propagates how does it look like along that you will find that, along depth sometimes it is tubular in nature, sometimes it is regular in nature, sometimes it is zigzag need process in a zigzag fashion.

So, if you are interested to know what kind of pitting has a occurred or what if you are interested to like interested to document the or measure the kinetics of pit formation a document the rate of pit formation. Then you have to be careful because you have to know the area fraction or volume fraction of pit as a function of time. And the area fraction of pit is available from the surface observation, but if you are interested to know the volume fraction of pit, naturally you have to go for cross sectional observation.

And subsequently find out the dimension of the pits or otherwise you have to go for some non destructive testing like a its a micro ct scanning by which you know the size and dimension of the peaks to a large extent and then you have to document as a function of time.

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So, this is very interesting and dangerous form of corrosion you have to be very much careful.

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So, few examples of pit formation are shown here for example, this is a top views of deep pits in types 316 stainless steel centrifuged head due to exposure in calcium chloride solution. So, you will find that pits are here and there and it is almost irregular in nature it has distribution is a regular it is not really uniform. So, somewhere it is very large somewhere it is a quiet less. So, depends on how there is local damage of the passive film which forms of the surface for protecting the layer.

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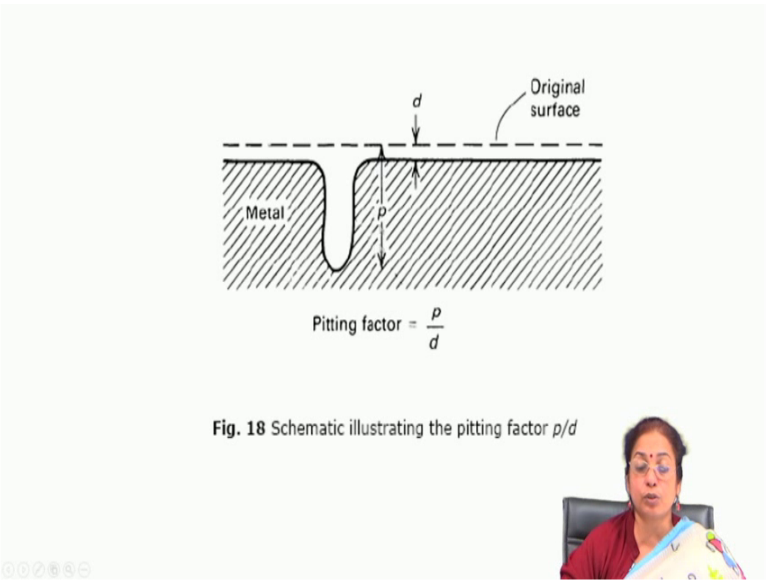

So, it is also evaluated by pitting factor; pitting factor is nothing, but if the rate is the ratio of overall pit depth total pit depth and also pit depth to the overall corrosion. So, whenever there is pitting at a naturally there is also normal (Refer Time: 04:56) corrosion factor because metal whenever you exposed to the environment naturally there will be general corrosion as well as pitting corrosion.

So, it is important that you know the pitting factor to a large extent, pitting factor is the ratio of the pit depth to the general corrosion depth. So, pitting factor is actually documented very nicely, so that you know the you have to some idea about the pitting corrosion tendency of the metal in practice.

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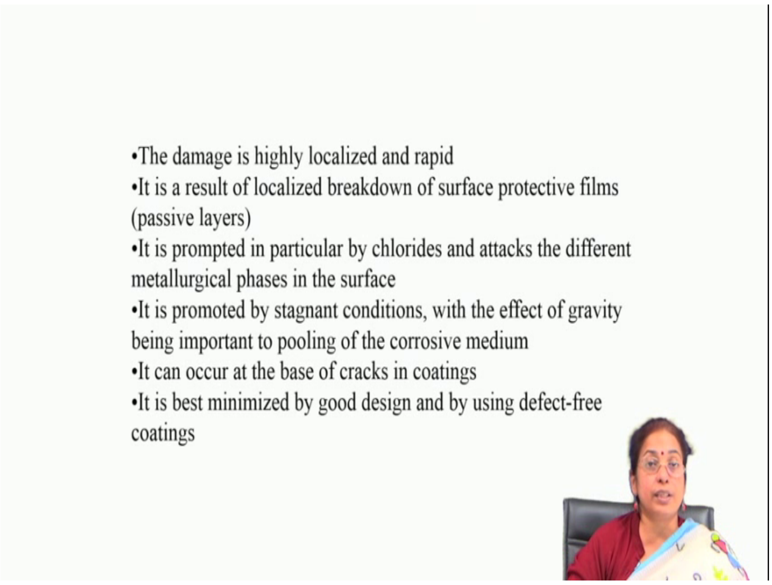

So, some of the characteristics of the pitting corrosion of that it is highly localized and rapid in nature particularly, the propagation rate is very rapid as I mentioned you that pitting corrosion again proceeds in two stages; one is pit initiation another one is pit propagation. Pit initiation usually is occurred in the sides of the for example, stress concentration region or may be in the region where there is local breakdown of the passive film in the presence of chloride contenting environment.

So, that particular site acts as a site for pit formation and pit propagation occurs, as soon as pit formation there is galvanic cell formation and subsequently propagation of pit occurs. So, this is highly localized and rapid and it is a result of localized breakdown of the surface protective film.

It is prompted in particular by chloride and attacks the different metallurgical phases the in the surface. It is promoted by stagnant condition with the effect of gravity being the important role and also it can occur at the base of cracks of coating. It is based minimize very good design and by using the defect free coating.

So, naturally you have to be very much careful and we have to choose the material which is which forms a highly protective film, particularly in that environment where you are looking to protect the surface.

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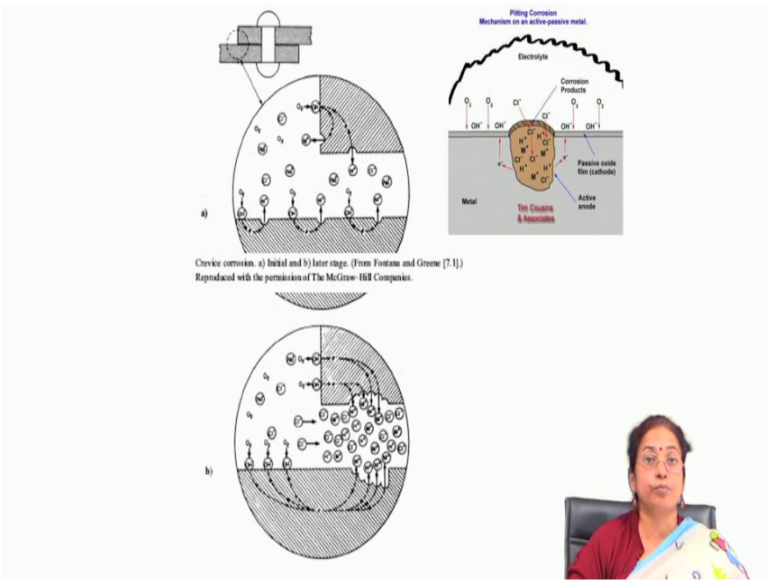

So, pit initialization as I mentioned you that pitting corrosion proceeds in two different stages; one is pit initiation and another one is pit propagation. So, this is the case and if there is crevice regent, naturally that further promotes or further aggravates the pitting attack rate. So, this is the case for non board combination which is exposed to the chloride containing environment, you will find that pitting corrosions starts at that particular point where there is actually local breakdown of the particular passive film.

So, what happens is that this is basically the shielded region, this is the unshielded region see that in the unshielded region there is lot of productive film formation, but in the shielded region there is local breakdown of the passive film. And as there is local breakdown of the passive film naturally you will see you will find that there is more attack of the expose surface and there is corrosion of the that particular surfaces and there is metal ion generation.

But there is depletion of the oxygen because of the differential aeration cell formation, you will find that and there as there is chloride in the environment you will find that the chloride actually goes on replacing the oxygen and then it basically it continues the typical corrosion process because of the presence of the chloride ion. The chloride process proceeds and as a result of which says autocatalytic generation of the chloride ion by the hydrolysis of the chloride. And as a result of which lot of chloride ion is auto generated in the inner part of the particular crevice and you will see that the corrosion proceeds to a large extent along the direction of the gravity.

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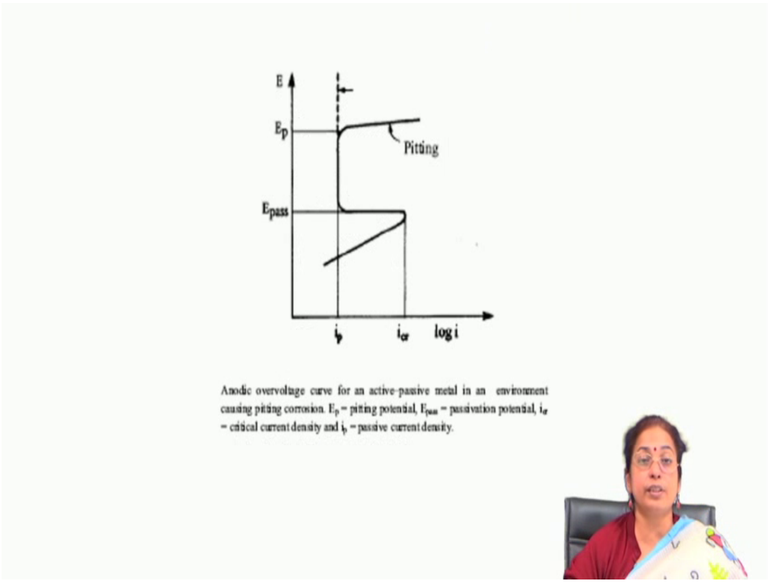

So, this particular pitting corrosion rate as I mentioned you that if you are interested to evaluate the pitting corrosion you have to know the area fraction of the porosity to a large extent with the help of typical microstructure analysis, otherwise you can also measure the pitting corrosion rate by electrochemical means.

So, in case of the component which has undergone pitting corrosion you will find that there is soft change in the passive to transfer passive zone and that particular sub that junction point or may be you can say that intersection between the passive and trans passive region potential gives you the information about E pit potential.

So, higher is the E pit potential higher will be the tendency of the metal or higher will be the resistance of the metal to pit formation. So, this pit initiation propose a pit initiation potential can be easily measured by electrochemical techniques and if you are interested to know the that pit propagation potential, then you have to do the cyclic polarization study. So, where you do initial that forward polarization as well as reverse polarization and usually reverse polarization potentials, if stops at a potential below that of the E corrosion potential you will say that it is the pit is very much prone to propagate.

But if it is above the E corrosion rotates here you can say that it is really, if it is below the E corrosion potential you can say that it is a very much prone to propagate, but otherwise if it is higher than that of E corrosion potential you can say that, even though there is pit formation pit is not to propagate table because it is highly protective in nature pit for (Refer Time: 10:22) which forms on the surface is protective, so it would not allow the pit to grow.

So, like that you can always evaluate the pitting corrosion resistance of any material. Otherwise you can also measure the Maslow's as a function of time Maslow's for unit area as a function of time in that particular specific environment. But as I mentioned you that due to pitting corrosion there is very less amount of material loss because the pit dimension is usually micrometer and it proceeds along vertical direction. So, possibly the pit depth might be 1 millimeter, 2 millimeter, 5 millimeter.

So, overall change in the width because of the pitting corrosion is significant insignificant that is compare to that of generic corrosion. So, if you are interested to measure the pitting corrosion resistance property of any material, you have to either evaluate it or find out the kinetics of the pit formation from the area fraction of pit or volume fraction of pit or otherwise by electro chemical means by the measurement of the E pit for the pit formation, as well as E pit for the pit propagation.

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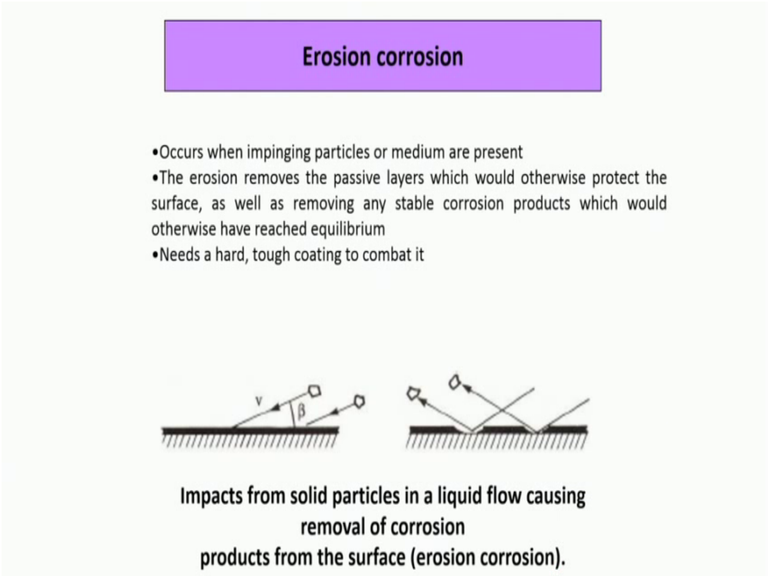

Now, next type of corrosion which is very important is that erosion corrosion. So, pitting corrosion and crevice corrosion their more or less similar in nature here the initiation mechanism is by micro galvanic cathode. But if you talk about erosion corrosion it is a little different in nature here also there is chance of the that particular breakage of that surface protective film, but because of the action of erosion.

So, as we saw earlier in the class of where in talks, where; where erosion phenomena was discussed, there we found that erosion occurs because of the mechanical interaction of the particular material or component with another environment which is flowing in nature.

So, there if the flowing environment is having lot of corrosive species you will see the condition of the erosion corrosion. So, erosion corrosion usually occurs when there is presence of the impinging particles or may be flow in the environment and the environment is corrosive in nature.

So, usually by the process of erosion the surface passive frame is removed and whenever it is removed naturally the phrase exposed surface get corroded to large extent because of again the galvanic cell formation between the freshly expose surface and that of protective surface.

So, that actually creates troubles that initiates the corrosion and as soon as there is initiation of the corrosion you will find that it propagates naturally, but here it is not like pitting corrosion, but it is erosion corrosion. So, it actually remains on the surface, as a result of which you will see on the surface there is lot of again material removal and if you see carefully you will find that it also looks like pitted surface, but its depth is much lower than that of pitting corrosion and in addition to that it is having certain degree of directionality.

So, if you see the pitted surface or eroded surface you will find that though it looks like the pitted surface but depth is much lower and also it is having certain degree of directionality. So, erosion corrosion is usually initiated by the mechanical interaction of the environment, maybe the impinging particle or maybe the liquid flow impinged eased on the surface whatever may be there is mechanical interaction which leads to damage of the typical stable protective film which parts on the surface and that causes further galvanic cathode and then increase rate of corrosion in the eroded surface.

So, if you are interested to compare the erosion corrosion you have to think of the development of a protective hard coating on the surface, so that hard and protective coating on the surface here is a lot because it actually reduces the tendency to erosion corrosion to a large extent.

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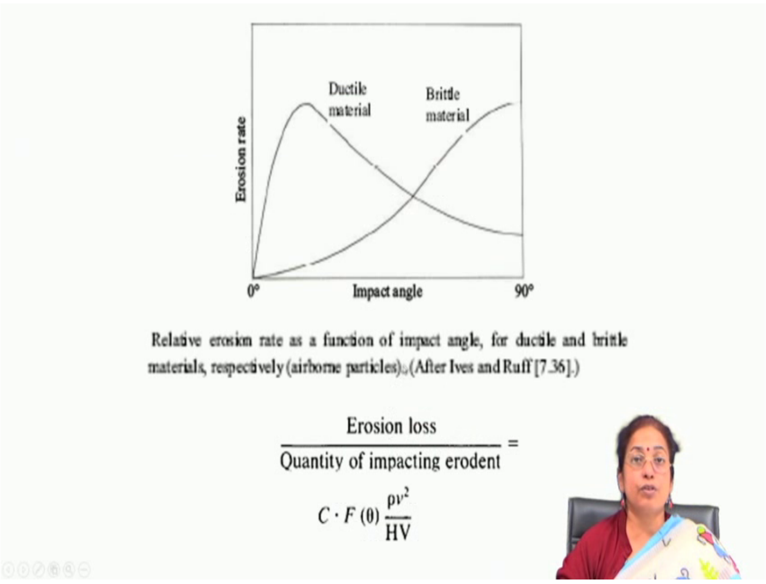

So, erosion corrosion is very much dependent on the not only that surface hardness and microstructure, but also depends on the impeachment angle. So, the flow if flow direction plays a for example, when the component is expose in natural environment in water, in pond or in case of river or in case of sea you will find that rate of attack is very much dependent on the direction of flow.

So, if the impact angle that is nothing, but the impact angle. So, for ductile metal you will find that usually at an angle of thirty degree or so, the erosion rate is maximum on the other hand it in brittle material the erosion rate is maximum at an angle of 90.

So, usually in ductile material it is very tough in nature. So, as a result of which erosion mostly occurs by the process of the typical; by the process of typical your information and then subsequent breakdown of the material because it is not really so hard, but it is highly tough in nature, ductile in nature. So, at an angle of 30 degree maximum amount of force is applied on the surface you will get maximum erosion.

On the other hand brittle materials are very much hard in nature. So, you will find that when the angle of impeachment is 90 degree at that angle usually you will find that is that this brittle material actually breaks down because of the action of the brittleness hardness as well as the amount of force that is applied on the surface also plays a very important role.

So, this particular mechanism is also kind of mechanical breakdown in the expose load is or may be applied load is exceeds the strength of the material. So, here actually another mechanism which also plays a important role that is cutting mechanism.

So, because of the cutting mechanism playing important role at 30 degree angle plays quite big role, but on the other hand brittle material that is only the amount of load applied on the surface or amount of energy associated with the particular impeachment plays very very important role and causes the that damage of the material. So, erosion loss is also very much it can be quantified in terms of erosion loss divided by quantity of the impacting erodent.

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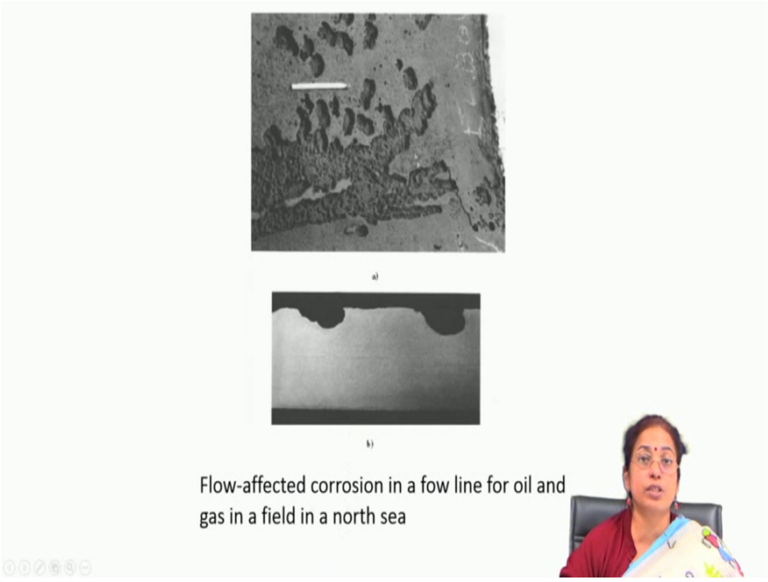

If you see the eroded surface you will find that this is the flow affected corrosion in a fluoride for oil and gas in field of north sea you will see that, on the surface lot of erosion is there they are very quiet big in nature is dimension very strong even millimeter, micrometer to millimeter; millimeter to centimeter event. And if you see the depth carefully you will see that along the depth of there is a certain degree of directionality, but it is not like a depth is not really so high as in case of pitting corrosion.

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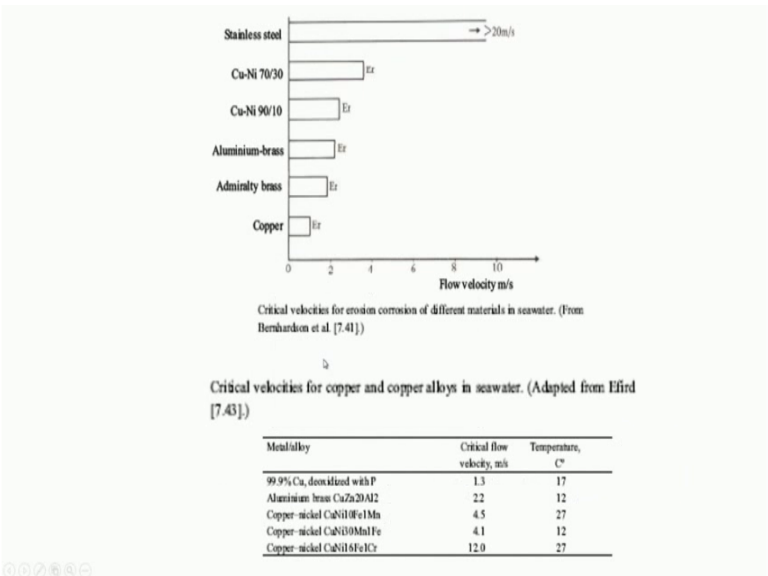

Metal/alloy	Critical flow velocity, m/s	Temperature, C°
99.9% Cu, deoxidized with P	1.3	17
Aluminium brass CuZn20Al2	2.2	12
Copper–nickel CuNi10Fe1Mn	4.5	27
Copper–nickel CuNi30Mn1Fe	4.1	12
Copper–nickel CuNi16Fe1Cr	12.0	27

Now, it is very important to know at which velocity the pitting corrosion will (Refer Time: 17:47) that crevice corrosion that erosion corrosion will start because if you are interested to choose the material for your choice, then naturally for the component of your choice naturally you have to choose it properly. So, that it does not get eroded in the particular environment or in that particular flowing environment.

So, this is the erosion critical velocity for erosion corrosion of different materials in sea water you will find that stainless steel actually can (Refer Time: 18:17) very large amount of flow as compared to that of copper nickel and aluminium brass and copper.

So, you are finding that as you go on increasing the hardness naturally the erosion attack tendency decreases or maybe the flow velocity required for the erosion corrosion actually increases. So, it is very important that if you are interested to protect the surface for erosion corrosion you have to apply a very thin hard layer on the surface. So, that it is protected.

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So, erosion corrosion of that you suffered by ash laden flue gas you see erosion corrosion can be so, high that it cause the damage at the corner point.

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Similarly, if you are interested to reduce it you can hard face it for example, hard face stainless steel plug and seat it is again a kind of though hard face, but you see that there is also erosion corrosion by high velocity flow through a narrow or if is created during that typical throttling operation. So, you will find that because of that a very large amount of energy is associated with that flow and it causes the damage of the component.

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The example of eroded tube inserts from the inlet end of fire tube boiler, the inserts were eroded by particle added flow gas which was forced to run as it basically enters the boiler.

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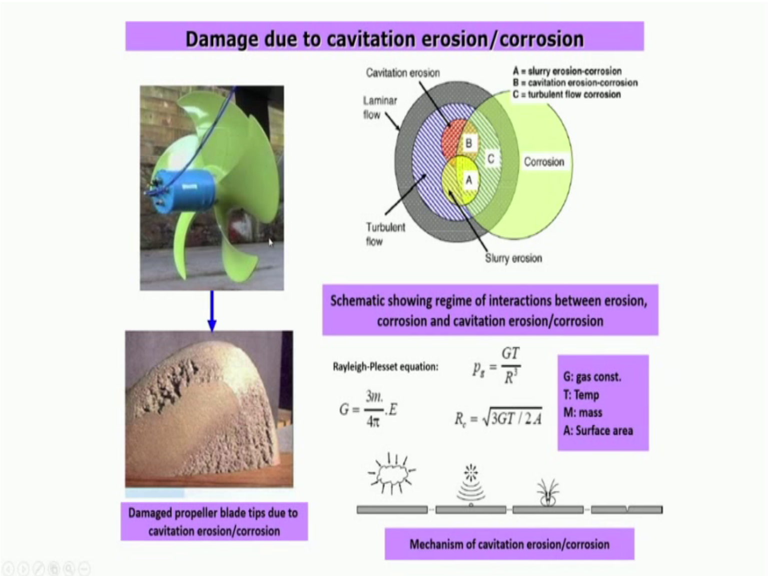

Now, one typical kind of for very interesting example of erosion corrosion is the cavitation erosion phenomena. So, normally erosion corrosion is usually observed in the constructed part its sea water or flowing in component in the sea water particularly if we just talk about the marine component that water pipeline or may be in the case of oil and gas pipeline you will find the erosion corrosion is very much prominent, its sea follows erosion corrosion is very much applied.

But if you see that particularly in the case of the component where, the component is kept in the media where there is large difference in temperature and pressure with the large difference in temperature pressure and velocity you will find that, there will be another type of erosion corrosion which is called cavitation corrosion which occurs in the component surface.

So, cavitation corrosion is the very dangerous form of corrosion in that regard there the rate of or energy associated with the impingement is so high that it causes cavity formation on the surface. Usually it is observed in the sea (Refer Time: 20:58) marine propeller where there is large difference in the pressure with the position of the component.

If you take the case for the marine propeller you will find that as its moves that is in some of the point the pressure is very high inner part of the propeller, but outer part of the propeller you will find that pressure is highly released. So, because of the large difference in pressure and also whenever it is flowing at a very large velocity there is also raise in temperature and also summer there is release of temperature too.

So, because of large difference in temperature and pressure you will find that the amount of gas which are usually deserved in the water media usually they basically changes somewhere to bubble and somewhere there in deserve condition. So, whenever the temperature is quiet high they are deserve wherever it is reduced they form the bubbles.

On the other hand where pressure is very high they are deserved, where pressure releases that they get there is bubble formation. So, lot of bubbles are present in the water media, so when those bubbles actually face the material surface they get collapsed and as soon as the get collapsed naturally you will find that in the collapsed region there is reduction in pressure.

So, that reduce pressure again cause a kind of that they are again some whenever there is reduction in pressure that particular pressure less region is get it get getting they are actually there will be lot of water jet which basically try to occupy that region and then try to maintain equilibrium.

And as a result of which you will find that lot of water jet basically get impinged on the surface of the component, where there is release in pressure because of blasting of the particular bubbles and they basically cause the material to get remove that much faster rate. So, if you see that cavitation erodes surface you will find that the material is eroded as a much faster rate leading to small small cavity formation.

And this can be quite dangerous and it can cause lot of material loss, if it is coated component the coating maybe lost at a much faster rate as compared to that of normalization corrosion. So, if you are using some component which is moving in that; which is moving in that particular flowing media you will find that cavitation erosion is a common form of erosion problem, cavitation erosion corrosion is the common form of the corrosion of the component.

Because as soon as there is erosion at a much faster rate natural the freshly exposed surface get corroded and then again eroded. So, there is local breakdown and then formulation this particular there is competition between breakdown and formation and because of the competition between the breakdown and few formation you will find that the as you go on increasing the rate of flow, as you go on changing the rate of the bubble formation that cavitation erosion problem also changes.

So, usually it is a function of temperature as well as the bubbles dimension. So, mass of the velocity of the particular liquid jet which is flowing on the which flows on the surface. So, this is a kind of combined action of temperature as well as pressure, as well as the mass of the liquid which actually gives the information about the kinetics of the cavitational erosion.

So, cavitation this is the particular pi chart we shows that corrosion as well as erosion as well as cavitation erosion zone, you will find that cavitational erosion zone is actually inside the turbulent part of that particular eroded erosion zone. And naturally when the component is having when the what media is having corrosive ingredient or corrosive species there that tendency for the cavitation erosion is maximum.

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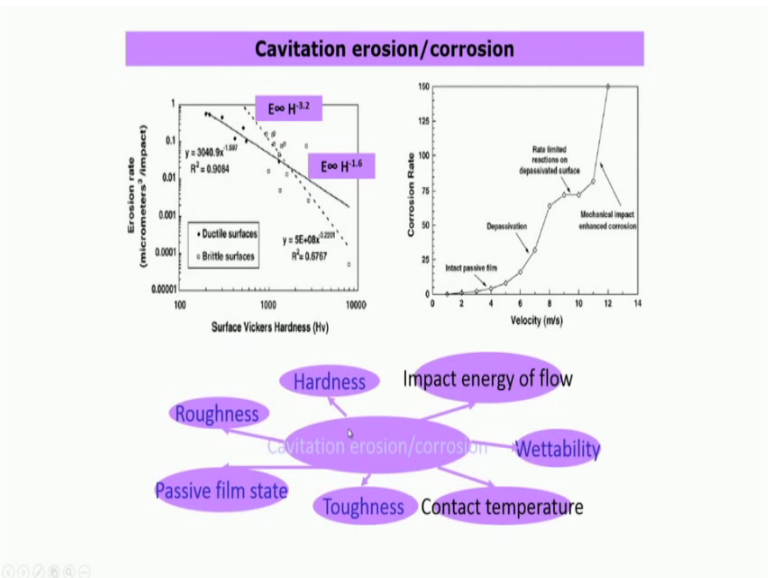

So, usually the cavitation erosion problem can be converted by increasing the hardness of the component, by increasing the toughness of the component, as well as reducing the wettability, the contact reducing contact temperature and also passive film state. So, if you are interested to increase the protectiveness against cavitation corrosion or minimize the tendency for cavitation corrosion you have to think of applying a very hard corrosion resistance coating. The coating after should be as minimum as possible, it should be less wettable.

So, that if you apply hydrophobic material that is always good actually because if it is hydrophobic natural wettability will reduced, as a result of which less what will be staying on the surface and which you will reduce the tendency for the particular cavitation erosion.

You can also increase the cavitation erosion or cavitation corrosion protectiveness or maybe minimize the tendency for cavitation corrosion by increasing the passive films strength. We apply some allowing element, so that the passive film which forms is highly stable in the environment. Toughness should be of great importance because if it is not a tough coating naturally, the coating will be damage very quickly with the help of the mechanical action.

So, if you see the corrosion rate as a function of velocity for different types of film you will find that, the passive film as a at very low velocity the passive film stable, but at a as you want increasing the velocity there will be the passivation. So, in between there will be de passivation and passivation phenomena at a particular critical velocity you will find that, it is no more stable because the breakdown dominates over the formation.

So, you have to think of the critical velocity for that erosion corrosion or cavitation erosion corrosion. So, higher is the critical velocity for the cavitation corrosion naturally higher will be the protectiveness of the material or you can use the material very nicely.

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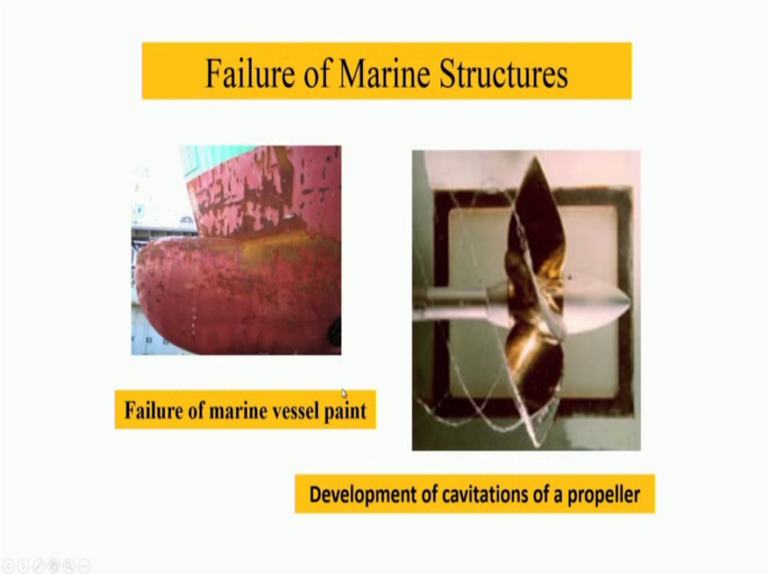

Few examples of cavitation corrosion includes, the failure of marine vessel paint, development of cavitations of a popular.

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They severely eroded tungsten carbide choke valve outer cage trim, so you see how badly it has been affected. So, big cavity formation are there all throughout the surface of this metal component.

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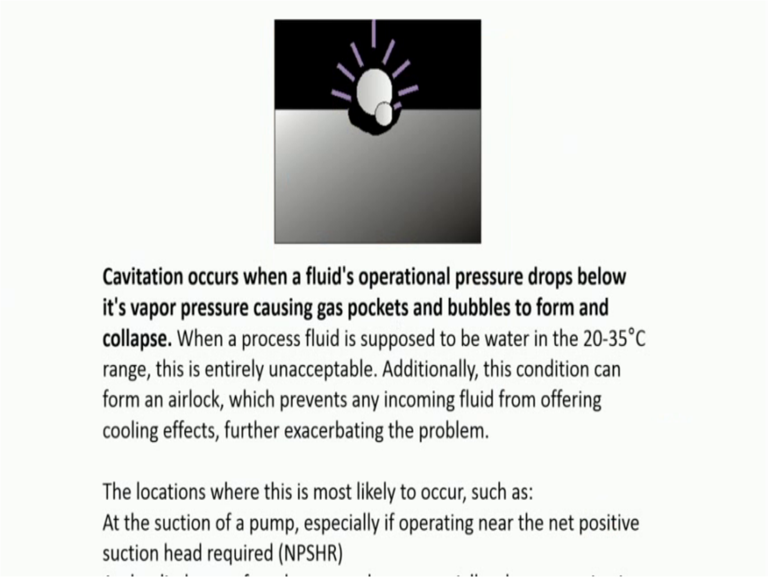

So, naturally this is important form of corrosion, so particularly when you talk about the seeds and then propeller. So, for these all components you have to be careful to compact the cavitation erosion as well as cavitation corrosion problem.

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And deaerator again this is the severe problem and it is the caste eroded limning in a diesel engine. So, we will find that external cavitation corrosion has occurred, even though it is cast iron, but the cavitation problems is so severe that it cause the damage of the component. So, these are few examples of the cavitation corrosion usually observed in practice. So, whenever you talk about cavitation corrosion it is very important.

So, in this talk we discussed about the different forms of corrosion particularly cavitation corrosion, erosion corrosion because they are again inter related to each other to some extent when there is no then they are always the in contact with it usually occurs in contact with the flowing fluid and when their flowing fluid is corrosive in nature. And cavitation particularly is predominantly observed for that cases where there is lot of bubbles in the flowing fluid, otherwise it is the phenomenon of simple erosion.

For both the cases it is very important that surface has to be corrosive as well as should be tough and hard. So, you can combat the probability of the both corrosion while applying thick a hard as well as tough layer on the surface in addition to having its very high corrosion resistance property.

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Thank you very much.