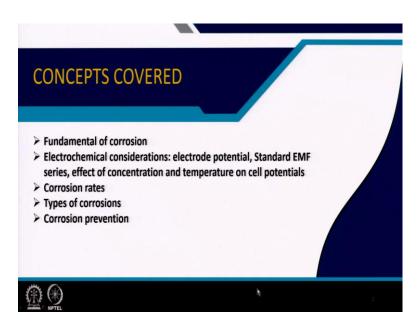
Non - Metallic Materials Prof. Subhasish Basu Majumder Department of Materials Science Centre Indian Institute of Technology, Kharagpur

Module - 11 Corrosion and degradation of non - metallic materials Lecture - 55 Fundamentals of corrosion, corrosion of materials

Welcome to my course Non-Metallic Materials and today we are in module number 11 Corrosion and degradation of non-metallic materials. And this is lecture number 55, where I will be discussing the Fundamentals of corrosion, and corrosion of materials.

(Refer Slide Time: 00:50)



Initially I will introduce the fundamental concept of corrosion; mostly we will be talking about the corrosion in metal. And in the next lecture, we will briefly introduce the corrosion or degradation behavior of ceramics, polymers and related materials.

So, this lecture is mostly devoted on various metal corrosion. So, electrochemical consideration will be taken care of, electrode potential will be introduced standard EMF series; then effect of concentration and temperature on cell potential that will be discussed. Then corrosion rates will be described, types of various corrosion pertinent to mostly metal that will be introduced and finally, how the corrosion can be prevented will be talked about.

#### (Refer Slide Time: 01:59)



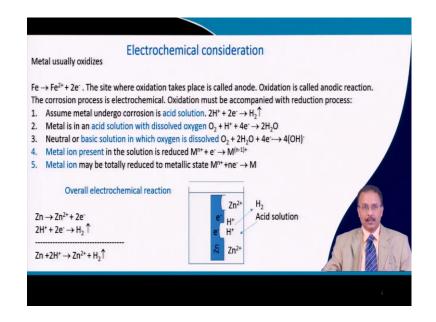
The topic you will find it an similarity already is there, when I talked about electrochemistry principles; then many of the concept what I will be describing today, you will find that is relevant to what you already know. So, in case of metal, materials loss by dissolution, we call it say corrosion; or by the formation of a non metallic scale, which is termed as oxidation, both will be talked about in this lecture and the following lecture.

In case of ceramic at low temperature, it is relatively resistant to degradation; but at high operating temperature, in particularly extreme environment, the corrosion cannot be prevented, otherwise they are corrosion free materials. In case of polymer, usually the term degradation is more appropriate. So, we will talk about three prominent degradation in the next lecture.

First one is dissolve in a liquid solvent, then second one absorb the solvent and swell and third one is UV radiation related degradation; these three things will be discussed in the next lecture. So, first let us take this electrochemical consideration. And as I told that this has already been outlined in earlier lectures when I discussed the galvanic cell, cell potential, Gibbs energy, concentration dependence, and etcetera.

So, electrochemical consideration are very similar to this those topics already covered. So, only the important outcome, important things will be highlighted in this particular lecture, which is relevant to the corrosion of metal.

## (Refer Slide Time: 04:11)



Now, metal usually as you know that they oxidizes; I can site an example, if you take the example of iron, then it oxidizes from metallic state to plus 2 state and it generates this electron. So, the site where this oxidation takes place usually we call it as an anode. And oxidation basically called as anodic reaction. So, the corrosion process in metal that is electrochemical in nature. And this oxidation is also accompanied by the reduction process.

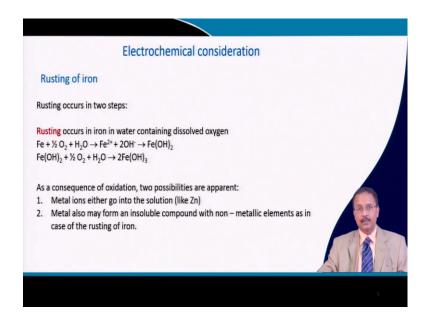
Now, the question is that, how this reduction takes place? So, if you assume that the metal undergo corrosion in an acid solution; then acid solution will have H plus ion, that will take up this electron which is coming out from the metal to form hydrogen gas. If the metal is in acid solution which is having dissolved oxygen in it; then this reaction takes place oxygen, H plus ion, and the electron that forms water molecule.

The third criteria could be that, it is a neutral or basic solution, where oxygen is dissolved. So, here this oxygen  $H_2O$  molecule and the electron that will form hydroxyl ion. It is also possible that the metal is present in the solution, which is reduced eventually. So, M plus is reduced to metallic M. And either two of them, either it can be a metallic M or it can reduce its balance. So, if it is  $M^n$  plus, it is  $M^n$  minus 1.

So, both type of reduction is possible. So, in case of zinc which corrodes quite easily, I can write the half-cell reaction for oxidation and in an acidic solution, the reduction reaction. So, basically zinc corrodes like this. So, here is an example that in acidic

solution, if you dip zinc; then it will eventually corrode and hydrogen gas will be generated as a reaction product.

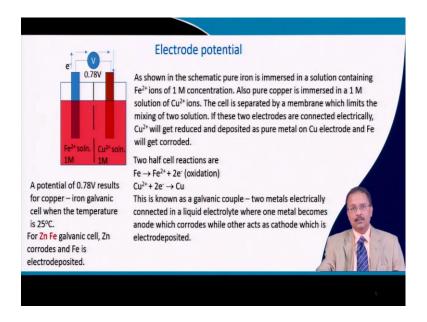
(Refer Slide Time: 06:48)



Rusting of iron is another example. So, rusting actually occurs in two different step. In the first step iron is oxidized Fe 2 plus and eventually it forms iron hydroxide. And then iron hydroxide that reacts with dissolved oxygen and  $H_2$  O or could be oxygen from the ambient, moist ambient. And eventually it forms iron hydroxide Fe(OH)<sub>3</sub>.

So, oxidation as you can see two possibilities are there, either metal ions they go into the solution, like that we observe in case of zinc. Or the metal ions can form an insoluble compound with non metallic elements as in case of the rusting of iron, which I just described.

# (Refer Slide Time: 07:55)



Now, look at this schematic here; pure iron it is immersed in a solution, which contains iron salt and the concentration of the salt is 1 mole. And also in the other half you have copper, which is also immersed in 1 mole solution of copper ions. And the cell that is separated by a membrane, which basically limits the mixing of this two solution.

Now, if this two couple is connected electrically and if you have a voltmeter here; then you will see that the copper will get reduced and this copper ion will get reduced and eventually it will deposit on this copper electrode and iron will get corrode. So, one can write the half equations for oxidation and for the reduction to get this metallic copper.

So, this kind of situation is called a galvanic couple, two metals which are electrically connected in a liquid electrolyte, where one metal becomes anode and corrode and other one acts as a cathode, which is basically electro deposited. This is also the principle of electro deposition. So, a very specific voltage about 0.78 volt this results out of this reaction or copper and iron galvanic cell at room temperature.

Now, if you consider a zinc iron galvanic cell, then zinc corrodes and iron is electro deposited. So, depending on the type of this two couple; one will get oxidized, and other will get reduced. So, it is not that always iron will corrode. In the later case, as you can see zinc corrodes and iron is electro deposited.

## (Refer Slide Time: 10:14)

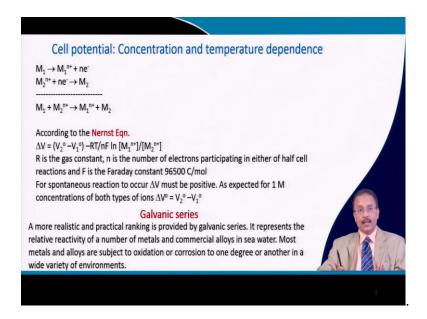
	Electrode reaction	Standard electrode potential V° (V)	Oxidation of metal M <sub>1</sub>
Increasingly inert (cathodic)	Au³+ + 3e⁻ → Au	+1.420	$M_1 \rightarrow M_1^{n+} + ne^{-} V_1^{o}$
	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771	Reduction of metal M <sub>2</sub>
	$Cu^{2+}+2e^{-} \rightarrow Cu$	+0.340	$M_2^{n+} + ne^- \rightarrow M_2 + V_2^{o}$
Increasingly active (anodic)	$2H^+ + 2e^- \rightarrow H_2$	0.00	$\Delta V^{o} = V_{2}^{o} - V_{1}^{o}$
	$Fe^{2+}+2e^{-}\rightarrow Fe$	- 0.440	
	$Zn^{2+}+2e^{-} \rightarrow Zn$	- 0.763	
	$K^+ + e^- \rightarrow K$	- 2.924	

Now, this is related to the standard EMF series. So, you can see the oxidation of metal that is basically given by this half-cell. And the voltage is taken as negative. So, this is I have denoted as negative V 1 0. For the reduction of the metal, this kind of reaction takes place and pure metal is electro deposited and the standard electrode potential in this case is taken positive.

So, the voltage difference is nothing, but V 2 minus V 1; that already we have described when we talked about Daniel cell you have seen it, zinc and copper we get a voltage out of it. So, depending on that, you can have an EMF, standard EMF series and this reaction the reduction of H plus ion to hydrogen gas that is called a reference point. And the voltage is taken as 0 at a particular temperature, which is typically 25 degree Celsius and 1 atmospheric pressure.

So, you can make easily a hydrogen reference cell, where inside a 1 molar solution of H plus hydrogen ion, hydrogen gas is bubbled on a platinum electrode and this reference is taken as 0. So, whatever is upper than that; so they are increasingly inert and whatever is below this reference series, that is increasingly active and act as anode.

#### (Refer Slide Time: 12:14)

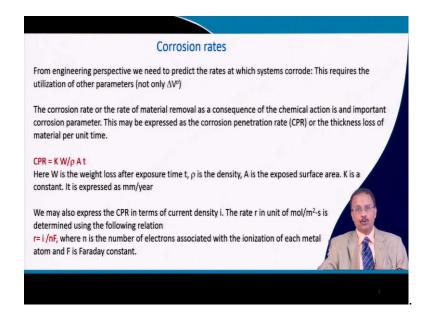


So, the half-cell reaction already I talked about for oxidation and for reduction. And this is your actual relation, actual reaction; this is a full cell reaction. So, if I apply the Nernst equation, which already I have described; then the generated voltage depends on the standard electrode potential minus this term, which is concentration potential R T by n F l n of the product concentration divided by the reactant concentration.

So, R here is the gas constant, n is the number of electrons participating in either of the half cell reaction and F is a Faraday constant, which typical is having a value of 96500. So, for spontaneous reaction to occur, the del V value must be positive. So, as expected for 1 molar concentration for both types of ion; if it is 1 molar standard case, then del V 0 is nothing, but the standard electrode potential  $V_2^0$  minus  $V_1^0$ .

So, a more realistic kind of practical ranking that is provided in terms of the galvanic series. So, it eventually represents the relative reactivity of the number of metal and metal alloys and electrolyte is typically sea water is considered. So, most metal and alloys they are subjected to oxidation or corrosion; the degree may vary depending on the where it is placed in the galvanic series. And a wide variety of environment can be chosen for this purpose.

### (Refer Slide Time: 14:17)

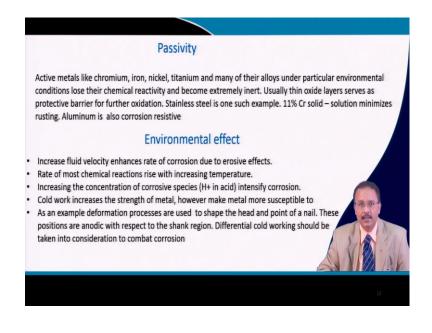


So, from engineering point of view, we need to predict the rate at which the system corrodes. So, this requires the utilization of other parameters. So, not only del V 0 is sufficient. So, the corrosion rate or the rate of material removal as a consequence of the said chemical actions that is important corrosion parameter. So, this actually may be expressed by corrosion penetration rate, which is abbreviated as CPR or the thickness loss of the material per unit time.

So, this corrosion penetration rate that is defined as a constant K and then W is the weight loss after it is exposed in that environment at a time t; rho is the density, and A is the exposed surface area. So, this is usually defined as millimeter per year. We can also express the corrosion penetration rate in terms of current density i. So, note that i is a current density. So, current per unit area and the rate unit is r.

So, r is your current density divided by number of electron and Faraday constant. And its dimension is mole per meter square per second and this is also used to define the corrosion penetration rate.

#### (Refer Slide Time: 16:11)



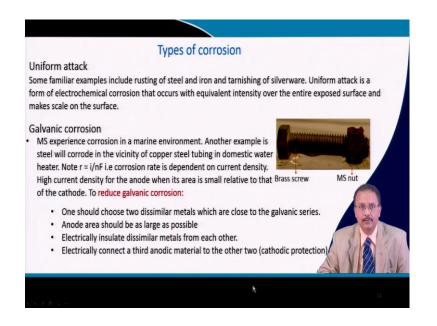
Active material like chromium or iron or nickel, titanium and many other alloys under particular environment condition, they lose their chemical reactivity and become extremely inert.

So, this is due to the fact, a very thin oxide layer that serves as a protective layer for further oxidation of this material. Stainless steel is one example; as you know in stainless steel about 11 percent of chromium that is made as a solid solution that minimizes rusting. Also aluminum is quite corrosion resistive material. So, environment has a strong effect on corrosion; usually the increase of fluid velocity, which is corrosive in nature that enhances the corrosion rate and this is called erosion.

So, material is lost because of this increased fluid velocity. So, rate of the most chemical reaction rise with the increasing temperature. So, increasing the concentration of the corrosive species; particularly if H plus iron is there in the acid, that also increases the corrosion. So, as an example of the deformation process are used to shape; for example, the head point of a nail and this is anodic in nature, so as compared to the shank.

So, different cold working also will have to be taken into consideration. So, if you do the processing of the metal, particularly cold working or doing some kind of special shape forming. So, those area are prone to corrosion.

### (Refer Slide Time: 18:24)



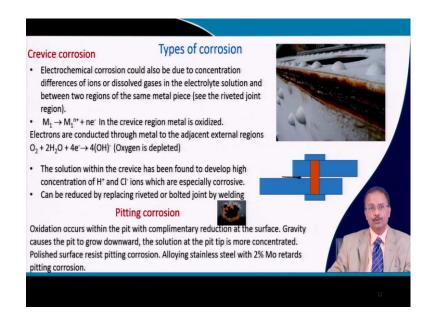
So, corrosion could be of uniform attack. So, the familiar example of rusting of steel and iron and tarnishing of your silverware; particularly if sulphur is there in the ambient, it forms silver sulphide and it forms a black color of layer on the shining glittering silver surface.

So, it is a uniform attack. So, attack that form the electrochemical corrosion that occurs with equivalent intensity over the entire exposed surface. So, it forms a scale. Next is the galvanic corrosion. So, MS tell that corrosion is quite; it is quite common in marine environment. Another example is steel will corrode in the vicinity of copper steel tubing in a domestic water heater.

So, here as I mentioned, the rate corrosion penetration rate is i by n F. So, the corrosion rate is dependent on current density. So, high current density of the anode will be more when its area is more exposed. So, to reduce the galvanic corrosion what I will do; I will reduce the area of the anode material, so that it reduce the galvanic corrosion. So, one should choose two dissimilar metal which are close to the galvanic series, so that the corrosion is minimized.

As I said the anodic area should be as large as possible, so that the I by a is small; so corrosion penetration rate is lowered. Eelectrically you can insulate the dissimilar metal from each other or electrically connect a third anodic material to the other one. And we will discuss that is called cathodic protection.

## (Refer Slide Time: 20:36)



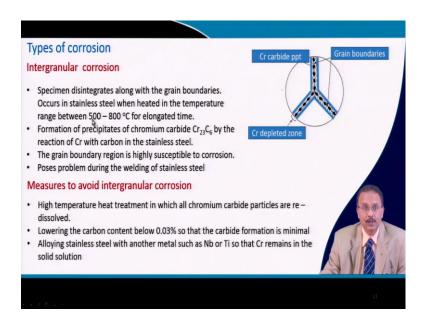
Crevice corrosion is also electrochemical corrosion that could be due to the concentration difference of the dissolved ion or dissolved gases in the electrolyte solution, which is snag stagnant between two regions. And it is particularly occur in the riveted, riveted joint like this. So, there is a small area as you can see. So, here the electrolyte becomes stagnant and here it give rise to the crevice corrosion.

So, initially the metal is oxide oxidized by this known reaction. So, electrons are conducted to metal to the adjacent external region and there the oxygen is there. So, oxygen is getting reduced and eventually the oxygen is depleted.

So, the solution within the crevice is therefore, develop a high concentration of H plus and chloride ion, which are especially very corrosive. And this can be reduced by replacing the riveted joint with welding; riveted or bolting joint can be replaced by welding to get rid of this kind of corrosion.

Another typical corrosion is the pitting corrosion. So, here oxidation occurs within the pit with a complementary reduction at the surface. So, gravity causes the pit to grow downwards. So, this is a small hole type of thing. The solution at the pit tip is more concentrated and usually the polished surface can resist the pitting corrosion. Alloying the stainless steel with say 2 percent molybdenum also get rid of the pitting corrosion of this type.

#### (Refer Slide Time: 22:43)

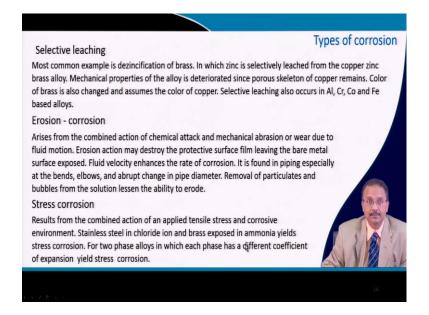


Inter granular corrosion is also operative particularly in case of stainless steel. So, here the particular material that degrades along with the grain boundary. So, when the stainless steel is heated at a temperature in the range of 500 to 800 degree Celsius for prolonged time; then it occurs the chromium within the steel, they form chromium carbide and then in the steel carbon is there. So, chromium carbide is formed and then they are precipitated along with the grain boundary.

So, this grain boundary region is highly susceptible to the corrosion and this poses the problem particularly when the steel structure is welding. So, the temperature is raised up to this level. So, then chromium inside the stainless steel reacts with carbon and then the weak the grain boundary to have this inter granular corrosion. So, as obvious to get rid of this high temperature heat treated, heat treating can be done.

So, that this chromium carbide particles they are re-dissolved. One can lower the carbon content below 0.03 percent, so that the carbide formation is also minimal. Or one can alloy the steel with some other material like niobium or titanium, so that the chromium remains in the solid solution and it does not react with the carbon in the steel.

### (Refer Slide Time: 24:28)



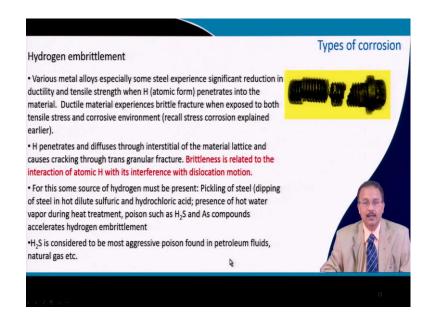
Selective leaching is very common for the alloy material; in brass is one example you know that copper and zinc alloy is there. So, selectively zinc is highly oxidizing material, so selectively it gets leached out. So, mechanical property is grossly deteriorated; because zinc is out from the structure and the resultant structure of copper they are porous in nature.

So, the color also changes from yellowish color, it changes to red reddish color due to the copper. So, selective leaching is also quite prominent for aluminum, chromium, cobalt, iron base alloy, it is also quite common. Erosion-corrosion already I have talked about. It arises from the combined action of chemical attack and mechanical abrasion, where due to the fluid motion.

An erosion action may be destroy the protective surface film leaving the bare metal surface exposed. And that thereby it is corrosive, environment will corrode the metal. Stress corrosion that result from the combined action of an applied stress and corrosive environment. And stainless steel in chloride solution or brass exposed to ammonia that yields to this type of stress corrosion.

For any two phase alloy in which each phase is having different coefficient of expansion, that also yield stress corrosion type of behavior.

## (Refer Slide Time: 26:11)

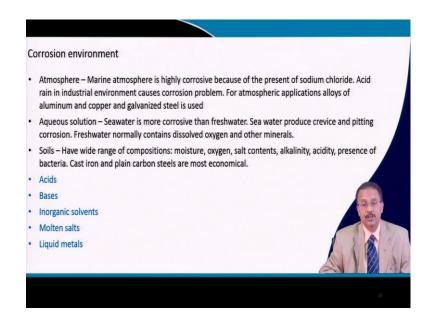


Another corrosive effect is hydrogen embrittlement. And various metal alloys especially some kind of steel experience significant reduction of the ductility and tensile strength when molecular form of hydrogen that penetrates into the material. So, the ductile material experience a brittle nature of brittle kind of fracture, when exposed to both tensile stress and a corrosive environment; it is something similar to the stress corrosion, which already I have explained earlier.

So, this is due to hydrogen penetrates through the interstitial of the material and causes cracking through the trans, mostly trans granular fracture. And it is proposed that this brittleness is related to the interaction of the atomic hydrogen and it interferes with the dislocation motion and therefore, I turned it to a brittle kind of behavior. So, some source of hydrogen must be present.

So, one example is the pickling of the steel. So, you know that steel is dipped into a hot sulfuric acid or hydrochloric acid; presence of hot vapor during heat treatment or if the poisonous material like  $H_2S$  and arsenic compounds are there, so these things will accelerate the hydrogen embrittlement. So, out of that  $H_2S$  is considered to be very aggressive poison, especially found in the petroleum fluid and natural gas.

#### (Refer Slide Time: 28:05)

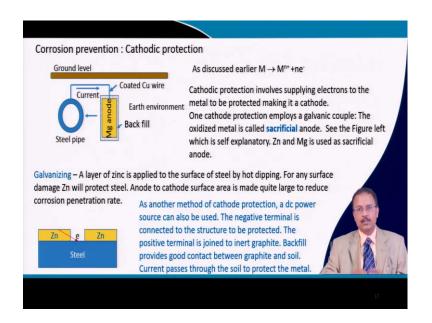


Corrosion environment is also important, particularly marine atmosphere is highly corrosive because of the presence of sodium chloride. Acid rain is another example in the industrial environment that creates this corrosion problem. So, for this type of application, usually atmosphere ambient dopamine ambient condition, condition usually alloys of aluminum, copper or galvanized steel that is. Aqueous solution also could be corrosive, sea water is more corrosive than fresh water.

Sea water produces the crevice corrosion and also pitting corrosion. And fresh water normally they contains dissolved oxygen along with the other minerals which also can be; because of this reduction nature, it can also corrode the metal. Soils could also be corrosive. So, it is having a wide range of composition, moisture content, oxygen content, salt content, alkyl alkalinity and acidity, presence of bacteria.

So, all these things can expedite the corrosion. So, usually cast iron and plain carbon steel are most economical to get rid of this environmental effect. Other than that different acid, base, inorganic solvents, molten salts, and liquid metals they also expedite the corrosion.

# (Refer Slide Time: 29:47)



So, cathodic protection is one good way to get rid of the corrosion and it is a very simple way. So, if you have a steel pipe here and which is prone to corrode; then cathodic protection involves supplying something which can supply electron to the metal and protect it. So, you will have to make it as a cathode. So, one of the cathode protection underground, it uses a sacrificial anode in the form of magnesium.

So, this magnesium or zinc that is used as sacrificial anode, so eventually it supplies electron to the steel pipe. So, it does not get corroded, it acts as a cathodic material and this thing it corrodes. And this is one way to get rid of the, it is one form of protection. Galvanization is another way.

So, a layer of zinc is applied to the surface of steel by hot dipping. So, for any surface damage, you know that the zinc will protect the steel. Anode to cathode surface area is made quite large to reduce the corrosion penetration rate whatever I talked about earlier.

So, as another method of cathode protection, one can apply a simple DC source one can use it; the negative terminal is usually connected to the structure that to be protected. The positive terminal is joined to an inert graphite, which is dipped into the soil with a backfill. So, the backfill it provides a good contact between graphite and soil. And current passes through the soil to protect the metal body.

# (Refer Slide Time: 31:48)



So, the study material is the book by Callister, chapter 17, corrosion and degradation of material and apart from that, the book by M G Fontana and D A Jones are also quite effective to know this principles.

(Refer Slide Time: 32:08)



So, in this particular lecture, we talked about corrosion principles; then electrochemical considerations; then electro potentials and standard EMF series; then we introduced the galvanic series concept; then corrosion rate was described. Then types of corrosion, there

are total eight types of corrosion we have briefly introduced and then finally, corrosion prevention in terms of this cathodic protection that was introduced.

Thank you for your attention.