Corrosion - Part II
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Lecture - 34
Oxidation of Metals and Alloys

Hello everyone. Today we will continue our discussion. And the today's lecture will be lecture 34. And we will start a discussion on oxidation of metals.

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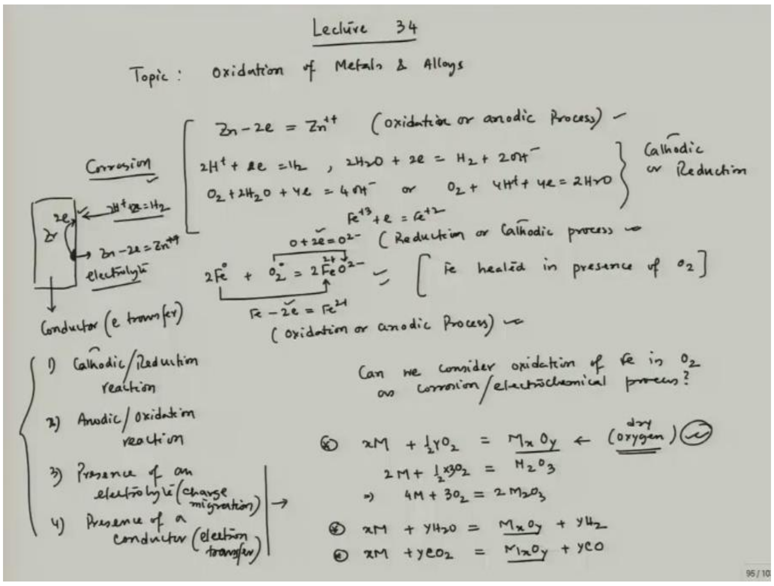

So, lecture 34. So, topic, oxidation of metals and alloys. Now, when we talk about oxidation of metals and alloys, we will concentrate as well as confine our discussion on gaseous oxidation of metals and alloys in presence of oxygen only. Of course, metal in presence of steam as well as if there is a possibility of CO2 presence, then also oxidation of metal can happen.

But we will talk about a metal reacting with gaseous oxygen and then forming metal oxide. That particular part, we will talk. Now, when we talk about oxidation, from our knowledge in corrosion, we have seen that oxidation means, when a metal leaves electron and goes to ions. And it is in basically the aqueous medium, where for example zinc in HCl solution. Zinc goes into solution in the form of ions, because oxidation of zinc takes place.

And we say that zinc - 2e. It goes to zinc++. This is oxidation or anodic process. Of course, in order to maintain neutrality, these electrons which are released by zinc must be consumed by some cathodic process, which could be hydrogen evolution reaction or oxygen reduction or water reduction. Even there could be possibility of metal ion reduction, like Fe^{+3} + e = Fe^{+2}.

So, we have seen that the counteracting cathodic process would be

$$2H_2O + 2e = H_2 + 2OH^-$$

There could be involvement of oxygen. It can happen like this.

$$O_2 + 4H^+ + 4e = 2H_2O$$

And there could be a process like

$$Fe^{3+} + 3e = Fe^{2+}$$

So, this entire process of cathodic or reduction process. In case of gaseous oxidation, like if I take a metal like iron; if I take it to high temperature in presence of oxygen, then iron can react with oxygen and form FeO or Fe2O3; or there could be a formation Fe3O4.

Then, if copper, I take it to high temperature in presence of oxygen, it can react with oxygen and form Cu2O or CuO cuprous as well as cupric oxide. Zirconium, it can form zirconium oxide, ZrO2. Titanium, it can form titanium O2. Or aluminium, it can react and form Al2O3. So, those are oxidation. If you see that a particular process like Fe + O2, it goes to FeO. Then, if I try to see if their oxidation number is zero now.

But when it forms and if I balance it, so balance would be like this. That case, I could see that oxygen goes to O2 - and iron goes to Fe^{2+}. Here also, you could see that Fe is releasing 2 electrons and forming 2 +. And oxygen accepts two electron and forming O2 -. So, that means, here also, in case of corrosion, this entire process we are talking about corrosion perspective, where zinc dissolution happens at a room temperature ambient temperature in HCl medium.

Where I can have oxygen presence in the form of dissolved oxygen or I can have ferric ion in the form of impurity. And then, this could be your only anodic process. And all those reactions can happen depending on the pH of the solution. Now, in the gaseous oxygen; so, that is, this reaction is iron piece is heated in presence of oxygen. And I could say that this is a dry oxygen.

So then, I can have this reaction. So, there also, I could see this is oxidation or anodic process. And this is reduction or cathodic process. And this counter balancing oxidation and reduction processes are required to neutralize its charges. Now, in this corrosion case, we are very clear that, on the surface of zinc; this is zinc surface. I can have + e = H; this cathodic process.

So, this electron comes from a place where zinc goes in the form of zinc + +, zinc + +. So, this place, we have dissolution; and this place, we have cathodic reaction. And electrolyte is basically acting as a medium where zinc ion is going, as well as hydrogen ion is flowing or migrating. At the same time, electrolyte is acting as a charged carrier in the form of ions. But if you see this electron, 2 electron is coming through the zinc piece.

So, this is the zinc piece. So, this acts as conductor for electron transfer. Fine. So, that means, that is what, this is an electrochemical process where we have 4 components: cathodic or reduction reaction; 2, its anodic or oxidation reaction; presence of an electrolyte; fourth is, presence of a conductor. Where, this migrates, charge migration happens here. And here, electron transfer.

So, we have 4 components of this corrosion cell or galvanic cell. Or even if we consider electrolytic cell, there also we have these 4 components. But here, I could see 2 components. One is this, another one is this. Now, where are the other 2 components? These 2 components we have to find out. Now, this is one query we have that, can we consider this oxidation process iron in oxygen as corrosion process.

Or I can say, corrosion or electrochemical process. So, we have to answer this particular query. But, at least one thing is clear that we could see 2 components, 2 parts of; if we see this 4 parts, at least 2 parts are there. So, we have to find out 2 more parts. In order to find out, we have to understand how oxidation takes place. So, before we go to that condition that, to that particular query that how oxidation takes place, we need to know that this is one way of formation of oxide.

There could be formation of oxide in the presence of water or steam. So, any metal, if I consider M, it can react with O2. It can form MxOy, where I can write it as a, this would be then half y and x. So, this is the balanced condition. For example, if I consider M2O3, that case, oxygen would be half into 3 + 2M. So, it will become

$$4M + 3O_2 = 2M_2O_3$$

So, that way, we can. So, this is a basically generalized formula. M2, M can react with H2O. This is reaction with oxygen. I could say dry oxygen. Then, if there is moisture, then that can also react. MxOy + H2. It can form H2. So, that time, I can say that this becomes; so, this will be the value. So, this is 1; this is 2. It can also have oxidation like M + CO2. Then, it can form CO.

So, I can balance it like y, y. Then you see that it is balanced. Okay. So, this is balanced now. And now here we, I put x. This x, y, these are the integers. So, this 3 ways, I can see that the same metal oxides are forming. But our concentration would be on this particular reaction. Now, if I try to now understand the mechanism of this reaction; as not mechanism; I would say that, what are the different processes that happen when oxidation takes place. Okay.

So, that we can see in a little while. But, if you see that this, if your formation, metal oxide formation, this oxide formation is a natural process. Why it is a natural process? We know that there is a factor called del G at a constant pressure, temperature.

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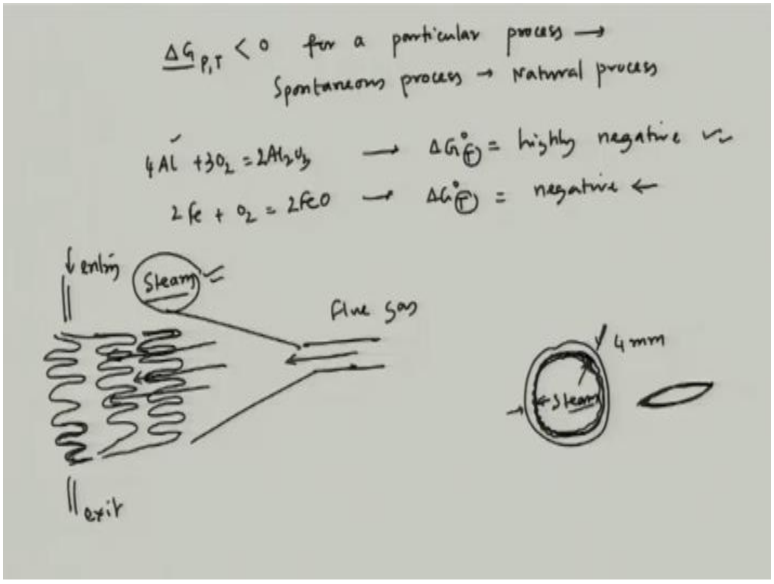

If that is less than zero for a particular process, we call it, this is a spontaneous process, spontaneous process. So, this oxidation reaction what we have shown here, these are having del G, which is free energy change negative. So, that means, those are spontaneous process. If those are spontaneous process, that means, those are natural process. Of course, this del G value for different process; if it is iron going to a FeO; iron going to Fe2O3 after reacting with oxygen; or aluminium going to Al2O3 after reacting with oxygen; all those processes might have a different values of del G.

For example, in case of aluminium,

$$4Al + 3O_2 = 2AlO_3$$

This is the balanced equation. That case, if I try to say delta G0. That means, the standard state. That means, the pressure to be kept as 1 atmosphere. That time, this value would be highly negative as compared to

$$2Fe + O_2 = 2FeO$$

This is the balance. Here, delta G0 T; if I try to see the same temperature, these 2 processes are compared. So, this will be negative. I am just putting a comparative statement. We will see later on with the help of Ellingham diagram, that; that time, we will be able to see the actual values of delta G0 T. That means, the temperature where that oxidation is taking place could be very highly negative for this case as compared to iron oxidation to FeO.

So, that time, we can say that aluminium has got a very, very high affinity to oxygen, as compared to iron. So, that means, if we keep iron and aluminium at a particular temperature in presence of oxygen containing 1 atmosphere pressure oxygen, then aluminium would try to get oxidized quickly. Because, it has a very, very high tendency to get oxidized, because its free energy change for the oxidation is highly negative.

So, that comparison will come later on when we talk about Ellingham diagram. But, at least we can see that this oxidation, gaseous oxidation is a spontaneous process. So, when we talk about spontaneous process, that means we have to also see, we have to also experience oxidation of structural components which are used at a high temperature. Now, this oxidation of structural components at high temperature will not be desired situation.

Because for example, if I have to design a material for turbine blade application, then that particular blade material must have high oxidation resistance. Otherwise, it will keep forming oxides on the surface. And that oxide would lead to, degrade its mechanical integrity. It can reduce its mechanical strength; it can reduce its creep resistance; it can reduce its wetting properties; all those mechanical properties will be negatively affected. Fine.

So, that means, oxidation; since we cannot avoid it, we have to find out something so that we can control it, we can reduce the oxidation. So, it is a same way like corrosion. Corrosion cannot be stopped; even oxidation cannot be also stopped. But, at least we can do something so that oxidation can be reduced for a, to a great extent, so that, that particular material can serve for a longer duration of time.

So, one, that means, we have to study oxidation behavior of metals and alloys. Similarly, this oxidation is, one part is, it leads to problem for the metal which is trying to give service at a high temperature, like turbine blades. There could be issues in heat exchanger. For example, sometime, in case of chemical industries, we have methane. So, that methane generation; methane can be burned.

And that methane, instead of leaving it to the environment, we can burn that methane. And then, we can get that heat recovered in the form of heating steam. So, the steam goes through a pipeline. And those are called heat exchangers. So, this pipeline; so, you have, its a kind of; you have a chamber, you have a big chamber like this. So, where from, you have those, where the flue gases.

We call it flue gas. Thus, gas is coming. This is burnt. And now, here you have a series, stacks of pipes. These pipes are there. Okay. So, now it is connected. One end is entry; another one is exit. Entry and then exit. So, through this pipe, we are sending steam. So now, when this flue gas is burned, it goes through this particular stacks of pipelines. Now, that process, this heat is then transferred to the steam. Fine.

So, that way, we are actually getting back useful heat by heating the steam, that heated steam can be used in other applications. Now, these pipes are made of irons, made of steel. Okay. So, these are cupronickel pipes. Those pipes can also get oxidized. Because, when steam is moving through this, outside surface might not get oxidized to a great extent, but inside wall might get oxidized to a great extent.

Now, if you have a wall thickness of let us say; if let us say the pipe wall thickness is 4 millimeter. So, this is, let us say 4 millimeter. This is the pipe through which steam is flowing. Fine. So, now internally, we have steam flowing. So, the steam can react with iron and form oxides. And these oxides will form inside wall. And then, gradually, this oxide will eat away the metal part.

So, the actual metal segment is thinned down. And these steam is also said has got some extra positive pressure. So, that pressure might fracture or rupture this outer wall, when this wall thickness reduces. So, that time, this rupture can happen in the form of fish mouth kind of fracture. So, if you see a fish, that when it opens the mouth, that time it looks like this. So, that kind of fracture can happen of that particular pipeline.

Once that fracture happens, then this plant needs to be shut down. Because, the purpose is not solved, because the superheated steam is actually going along with the flue guess. So, now this happens because of the severe oxidation of the inner wall. So, this is the problem. So, that means, we could see that, whenever some material is chosen; for example, in case of aerospace applications.

Now, copper alloys are used for making combustion chambers. Fine. So, that alloy must process oxidation, sufficient oxidation resistance or resistance to the chemical or the fuel that is being burned over there. Otherwise, oxidation can lead to failure of that particular combustion chamber. Similarly, in many other cases, we need high temperature applications. Even, for example, thermal power plant.

We need application where high temperature is experienced. Even furnaces; if you see induction furnace; if you see any other furnaces. So, the outer wall is made of metals, steels. And the inner wall, we always cover with refractories, so that the outer wall does not get much of heat. But even if gets heated, oxidation can happen. But that material gives a sufficient oxidation resistance, so that, that furnace wall can withstand the load that is there inside.

So, that way, oxidation needs to be studied. And it is a, it is an important aspects of material choice. Like for example, if you have to select material at high temperature, you have to have oxidation properties of that particular metal. So, that way, oxidation is an important aspect to analyze. Now, coming to the processes that could happen on the oxide, on the metal surface. We can have a series of processes.

Like, we can have oxygen when the metal is exposed to oxygen. Oxygen can get absorbed on the surface. There could be nucleation of; and then, it will be followed by nucleation of metal oxides. And then, the coverage of the metal oxide film, by a metal oxide film over the metal surface. There could be diffusion of atomic oxygen. There could be dissolution of atomic oxygen with the metal.

And then, once that limit of solubility of that atomic oxygen in that particular metal exceeds, there could be internal oxidation. Now, oxide might have a different thermal expansion coefficient, rather than, as compared to the metal. At a high temperature, oxide can crack. It can form micro crack; it can form macro cracks. And then, accordingly, we will have a difference in oxidation tendency of different metals. So, we will talk about different stages of oxidation in our subsequent lectures. So, let me stop here. Thank you very much.