Corrosion - Part II
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Lecture - 35
Different Stages of Oxidation and Pilling-Bedworth Ratio

Let’s start lecture 35.

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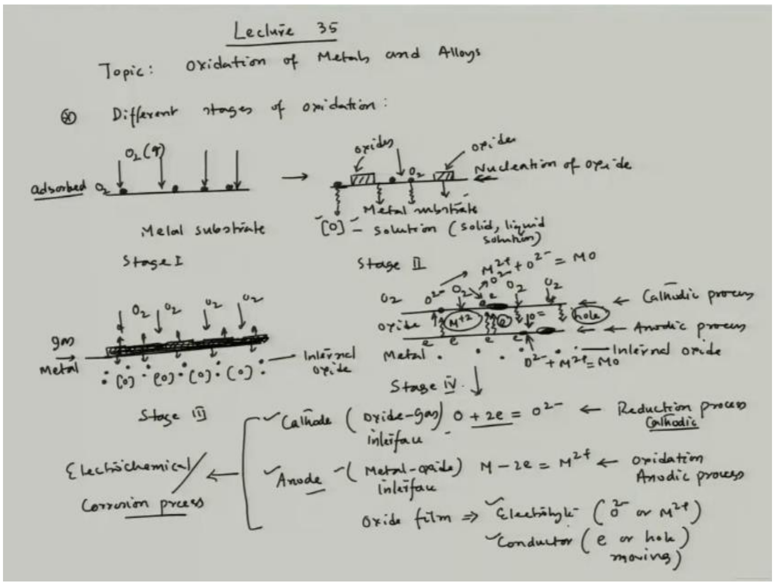

Lecture 35

Topic: Oxidation of Metals and Alloys

⊛ Different stages of oxidation:

Electrochemical / Corrosion process ←

✓Cathode (oxide-gas interface) $O + 2e = O^{2-}$ ← Reduction process Cathodic

✓Anode –(Metal-oxide interface) $M - 2e = M^{2+}$ ← oxidation Anodic process

Oxide film ⇒ ✓Electrolyte (O^{2-} or M^{2+})
✓Conductor (e or hole moving)

And topic, oxidation of metals and alloys. Now, in our last lecture, we started discussion on oxidation. And we could see that oxidation poses lot of issues for a material to be used at a high temperature. And that is what we need to analyze oxidation. And then we started talking about different stages of oxidation. Now, if we see different stages of oxidation. So, whenever a metal is exposed to a gaseous oxygen at high temperature, let’s say this is the metal substrate.

So, now you have oxygen, gaseous oxygen. So, now they are coming in contact with the metal surface. And when they come in metal surface, then oxygen can get adsorbed. So, this is adsorbed oxygen on the surface. So, I can have those adsorbed oxygen on the surface. Now, this is the first step that forms. This is the step 1. Now, when this adsorption happens, then the stage 2; what is going to happen?

The stage 2, this is the metal substrate. So then, there could be local oxide formation. We can call it as nucleation of the oxide. And of course, this oxygen adsorption of oxygen on the metal surface keeps on going on, keep going on. This adsorption, other exposed area adsorption takes place. Now, when it happens, that time, there could be possibility of dissolution of oxygen in the metal.

So, this is dissolution of oxygen. And that forms solution. So, it could be either solid solution or liquid solution, depending on the state of that particular metal. If it is a solid state, then of course solid solution happens. If it is a liquid state, liquid solution happens. But at least I could see, we could see that the oxygen can diffuse in. And then, that can go into the lattice and form solution.

Now, so, that means, we have adsorption, we have nucleation of oxides and we have dissolution of oxygen. And those dissolved oxygen is in the solid solution, if we consider the solid metal exposed to the oxygen. Now, this is stage, step 2. Now, or we can say stage. Stage 1; instead of step, we can say stage 1, stage 2. Now, when this oxygen is going in and then forming solid solution, now we know that this solid solution is possible from 0 to 100 % in case of isomorphous system.

For example, nickel and copper, they are isomorphous. So, that is what nickel can take as much of copper. Even copper can take as much of nickel. So, there is no limit. But, there are situations where metal can, one metal can take another metal to a certain limit in the solid solution. Like aluminium; when aluminium and copper is mixed up to around 5.65 weight percent of copper can go into aluminium.

And if we go beyond that, when they are solid, this aluminium is solid. If we go beyond that, copper would come out and then form Al2Cu. Of course, this process has got different stages. If we start with 4% copper in aluminium, so then if we cool it down to, quench it down to room temperature. If we hold it at room temperature, the copper concentration that can be possible in the solid solution of aluminium is much less than 4% of copper.

So, the remaining copper will try to come out in the form of different precipitates. And if we see that aluminium copper system, the precipitates are varied precipitates, there could be GP-zones, there could be theta double prime, theta prime. And then finally theta, which is the equilibrium precipitate. It is Al2Cu. So, those phases are forming because aluminium is no longer holding that 4% of copper, which is possible at a higher temperature.

But at a lower temperature, it is not possible. So, that means, there is a limit up to which one metal can take another metal in its lattice. We call it a solid solution. Similarly, in case of metal oxygen situation, a metal can take oxygen in its lattice and form solid solution up to certain extent. So, if the oxygen content goes beyond that extent, then oxide will come out. So, that means, when this oxygen dissolved oxygen is going in, this oxygen, if it exceeds the amount of oxygen that can be held in solid solution in that metal, then oxides can form.

So, this oxides can form inside this interface, the interface between gas and metal. So, inside that, oxides can form. So now, if I consider the stage 3; so, we have nucleation of, more nucleation of oxides. At the same time, oxides can also grow. Okay. So, these are oxides. Fine. These oxides can grow also. It can grow towards this. At the same time, it can grow towards this; or it can go this way also, depending on how the diffusion of species takes place inside the oxide.

Now, at the same time you have dissolved oxygen which is in the solid solution. So, they can form internal oxides. So, these are internal oxides. And this, of course, this is the gas metal interface. And oxygens of course, it is keep coming towards this. Now, this internal oxides can happen. Now, this is stage 3. At the same time, there could be possibility that the entire surface is covered by oxides.

Now, once it covers by, this particular oxide covers the metal surface; now, we can have 2 more interfaces, 2 interfaces. Now, this is oxide. This is oxygen. This is metal. So, we have 2 interfaces. Now, of course, there could be internal oxides. This is internal oxides. Now, here we have oxygen. Now interestingly, through this oxide, I can have metal ion flow; or I can have oxygen ion flow; I can have electron flow; I can have hole flow.

So, we will come to know this hole as well as electron, because oxides are not a stoichiometric compound. Rather they are non-stoichiometric compound. And because of this non-stoichiometry, oxide can be either p-type or n-type. In case of p-type, the charge transfer happens through hole. And in case of n-type, charge transfer happens via electron flow. So, that is what I have put, hole and electron.

So now, these processes can take place. Now interestingly, if I try to analyze this processes, oxygen, since through the metal oxide film, I can have O 2 - ion transfer. Now, that means, at this interface, I would have; that means, interface, that means oxide gas interface. I will, in order to form O2 -, it must take 2 electrons. So, O2 -. Now, at the same time, in order to form M2 +.

That means, it can happen at metal oxide interface, where metal can release 2 electron and form M2 +. So, that means, here it forming 2 -; and here it is forming 2 +. Now, interestingly, if you see this, this is cathodic or reduction process or cathodic process. And this is oxidation or anodic process. Fine. Now, since this interface acts as a surface where this oxidation takes place, I can term it as anode.

And this particular interface where cathodic reaction happens, we can term it as cathode. Now, this oxide has to grow. It can grow over this surface or it can grow over this surface; depends on which one is diffusing faster. Now, if metal ion diffuses faster than oxygen ion and it can reach to this interface before oxygen and pushes through this particular oxide film. So, this metal ion comes.

And by the time it, once metal ion comes over there, it finds 2O2 - ion. Because of that electron acceptance process, the oxide can form. So, these 2 combine. M2 + + O2 -; it combines and form MO, that oxide film happens or oxide film goes on this surface. Now, with oxygen ion diffusion through that oxide is faster than metal ion diffusion, then these oxygen oxide oxygen ion comes over this surface before it goes to the other surface, metal + 2 goes to the other surface; that means, oxide oxygen surface.

Since this diffusion is faster, so the, it will come over here, oxygen 2 - will come over here. And then, it reacts with metal 2 + and form MO. So, that means, oxide can grow over this particular interface; oxide can grow over this particular interface, depending on which species is diffusing faster. Now, at the same time, so this anodic process happens at this interface anodic process.

So, that means, electron is left here. So, these electron can flow to the other surface. And it reaches here. It accepts these 2 electrons and forms O2 -. So, that means, here we have cathodic process. So, that means, this oxide film is acting as an electrolyte through which O2 - or M2 + are moving. That means, where the, we know that electrolyte, it holds that ions and it also helps in migration of ions.

So, that means, oxide is acting as electrolyte. Now, these electrolyte, it also flows charges. The charge is in the form of electron or it forms on the positive hole. So, those are the charges. Those charges, it can also migrate; so, through that electrolyte. So, this is also acting as conductor, since electron or hole, they are migrating or moving. Now, we could see that we have cathode; we have anode; we have electrolyte; we have conductor.

And if we go back and try to see different stages of corrosion or different parts of corrosion. So, we have cathodic reaction; anodic reaction. That means, we have cathode, anode presence of an electrolyte; and presence of a conductor. Here also, I could see that we have all the 4 parts. So, that means, this is also electrochemical. Or we can say that this is also a corrosion process.

Since metal is going into ion forms, there the metal is not dissolving into the electrolyte, in the electrolyte. Rather, it is forming a phase which is oxide phase. Now, this is a stage, I would say this stage 4. This is stage 4. Now, when this oxide film is forming, if I consider this oxide film.

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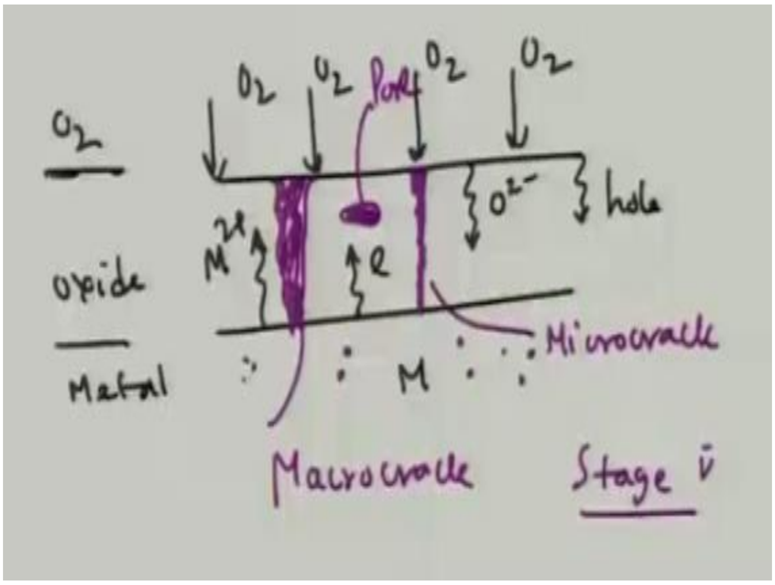

This is the metal oxide oxygen. This is the interface. These are the 2 interfaces. Now, that time, when oxides oxide is growing; since oxide is less plastic as compared to the metal, there could be a possibility of crack formation in the oxide. So, we have metal ion flow; we have oxygen ion flow; we have hole, hole transfer; we have electron transfer. This is metal; oxygens are coming.

So now, so these process are taking place. There could be a crack formation, micro crack that can generate. These are the micro crack. This micro crack can form because of, that particular, because that particular oxide is not as plastic as metal. And as, then when it grows, it can lead to a stress on the oxide; and then oxide can crack. This micro crack, there could be possibility of macro crack.

This macro crack also possible. There could be possibility of; this is the macro crack. This is the micro crack; this is the macro crack. There could be possibility of pores. And of course, internal oxidation is going on, because oxygen is dissolving in metal. It is forming solid solution. It exceeds that limit and forms internal oxides. So, that means, we have formation of holes, pores.

We can have formation of micro crack; we can have formation of macro crack. At the same time, those processes like diffusion of metal ion; diffusion of oxygen ion; flow of charges in the form of positive hole or electron; oxygen coming to the oxide surface now; those entire, all the process are going on in parallel. Okay. So, this is a stage 5. So, I can say that this is a stage 5.

So, these are a kind of different stages of operation. So, though it looks not much of complicated, but these different stages can be mixed up. And those stages could have a various other influencing factors. Like this is a pure metal situation. If there are alloying contents, then this stages can differ, can vary. Depending on the alloying content, this diffusing species, they can be varied diffusing.

For example, if we have one type of alloying element, that time diffusion can be sluggish. If we put another kind of alloying element, diffusion can be faster. So, all those situations can take place. We will discuss one by one. But at the current stage, we can see that there are 5 stages. And stages, if we try to see, oxygen adsorption; nucleation of oxide; oxide growth; film coverage over the metal surface; then diffusion of ionic species as well as charge species; and then finally, we have defect generation in the oxide film.

Of course, there could be possibility of internal oxidation also. So now, if we try to look at this different stages; and once we look at different stages, we could see that oxide is always forming on the surface. Now, when oxide is forming; in the beginning, the oxidation is fast, definitely. Because metal is exposed to gaseous oxygen, oxidation becomes fast. But once this metal surface is covered with oxide film, then, the oxidation process, the further oxidation will be decided by this oxide film.

I mean to say that, the nature of oxide film will then ensure, whether the further oxidation would be sluggish or further oxidation would be faster. Now, for example, one case, for example, in case of aluminium oxide, Al2O3. So, that oxide is a very, very strong oxide. It forms over the surface. But, at the same time, it does not allow further diffusion of those iconic species.

And if we stop those diffusion of ionic species, then of course, we are stopping oxidation. So, that means, it will form a film, but it will not allow further oxidation. That is what aluminium is a; even though it has, aluminium has got a very high affinity to oxygen, but it protects the underneath metal quite nicely, because of that impervious aluminium oxide formation. Similarly, chromium. Okay.

Chromium also forms a chromium oxide layer that prevents further oxidation, because it actually prevents further diffusion of those ionic species. Because, in the beginning, that reaction happens in the nascent condition, oxygen reacting with metal and forming metal oxide. But once the film is forming, the metal surface is covered with metal oxide. Then the further oxidation will be decided by how quickly those diffusion of species takes place.

And this diffusion of species means, the metal ion or oxygen ion. At the same time, we have to also look at the charge flow. Because, in case of corrosion, we have seen that, even though we have a great tendency of a metal to get corroded, if we can increase the resistance of the path of charge flow, then corrosion rate can be reduced. Just like, if we have zinc; if we put it in HCl, corrosion would be very high.

If we just remove HCl and put it in a H2O, then the corrosion rate would be very low. Okay. Because, H2 has got a less conductivity as compared to HCl. So, that case, we can have less corrosion. At the same time, if we have a dry condition, then we do not have electrolyte. So, all those cases, what we are doing? We are actually increasing resistance to the flow of charges or flow of ions.

So, here also, if we can improve resistance in that oxide film to the flow of ions or charges, then of course, we can control the oxidation. So, that leaves us a great possibility that, somehow if we can look at oxide, the, and try to do something with that oxide; then, of course, we can prevent further oxidation. And interesting part is, we cannot avoid oxidation, because oxidation is a thermodynamically spontaneous process.

And it is a natural process. So, if we cannot stop that natural process, let’s do something on the oxide, so that we can influence the diffusion process or the charge flow process. Now, this particular aspect that, how to improve resistance to diffusion or resistance to diffusion resistance to charge flow; those aspects are complicated. So, in the beginning, when people tried to understand that how to improve oxidation resistance or how to understand that this metal might give oxidation resistance at a high temperature; that time, one particular parameter came up. That parameter is called Pilling-Bedworth Ratio.

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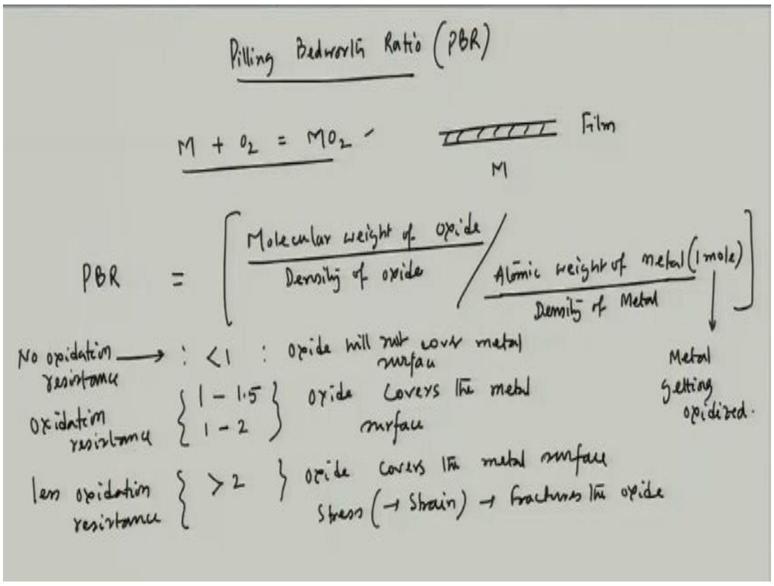

Pilling Bedworth Ratio (PBR)

$M + O_2 = MO_2$

$$PBR = \left[\frac{\text{Molecular weight of oxide}}{\text{Density of oxide}} \Big/ \frac{\text{Atomic weight of metal (1 mole)}}{\text{Density of Metal}} \right]$$

Metal getting oxidized.

No oxidation resistance → : < 1 : oxide will not cover metal surface

oxidation resistance { 1 – 1.5 / 1 – 2 } oxide covers the metal surface

less oxidation resistance { > 2 } oxide covers the metal surface
Stress (→ Strain) → fractures the oxide

So, if I try to understand this, if we try to understand this Pilling-Bedworth Ratio, let’s say

$$M + O_2 = MO_2$$

Since oxide is forming and forming a film; so, that means, this is metal and let’s say it is forming a film. So, when I form a film, that film, either it can cover up the entire surface or it may not cover up the entire surface. Now, whether it will cover up the entire surface or not, that will be decided by the volume of the metal oxide that is forming on the metal.

Now, the amount of metal, when it gets oxidized, that forms metal oxide. And if the volume of that metal oxide is less than the volume of metal that is being consumed for oxidation; then, of course, metal surface will not be covered up completely by the metal oxide. But, if the volume of the metal oxide is more than the volume of the metal that is being consumed by oxidation, that time, of course the metal oxide will fill up the, will form a continuous film on the surface.

So now, that particular aspect can be taken as a kind of thumb rule, that yes, if we have a kind of a thumb rule or that can be converted into a parameter. By looking at the parameter, one can charge that, yes, this particular oxide can cover up the surface. So, that is what this Pilling-Bedworth Ratio has been designed. So now, here what it says that, if this is the reaction that is happening and if we assume that the metal oxide is forming on the surface and it is not evaporating or melting.

So, that case, molecular weight of oxide divided by density oxide divided by atomic weight of metal divided by density of metal. Now, interesting part is; when I am talking about atomic weight of metal considering 1 mole of metal getting oxidized. So now, every time, whenever we try to find this ratio, we have to consider 1 mole of metal going into metal oxide.

So now, this would be, we call it as PBR or Pilling-Bedworth Ratio. So, this is PBR. Now, if this ratio is within 1 to 1.5 or some people considered as 1 to 2. If this ratio is between this value, we can say that the oxide covers the metal surface. Since oxide covers the metal surface, that is what we have lost the direct contact of oxygen with the metal. And we assume that, that metal will be protected.

But if this particular issue is less than 1, of course, oxide will not cover metal surface. So now, we will not have, in this particular case, no oxidation resistance. And in this case, we will have oxidation resistance. But, if this ratio goes beyond to; though oxide covers the metal surface; but, it generates stress. And which leads to strain. Since oxide is not plastic, this strain fractures the oxide.

And once it fractures, it opens up the fresh metal which react with the gaseous oxygen and goes into further oxidation. So, we will say, the less oxidation resistance. And remember, this is, there is, this particular thing, only is based on whether the metal oxide covers at the surface or not. So, we will continue our discussion on this Pilling-Bedworth Ratio and try to do some calculations to see the behavior of metal, whether that particular oxide will be protective or not. So, let’s stop here. Thank you very much.