Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 36
Broad Subject: Oxidation and hot corrosion, Pilling Bedworth ratio, Thermodynamics of oxidation

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Today we'll discuss oxidation and hot corrosion phenomena, so today's discussion is oxidation and hot corrosion, and this oxidation means mainly reaction of metal with oxygen at high temperature. So let us first get into oxidation, the first scientific studies on oxidation it's basically from ratio people can determine, people is to determine whether the material has very good oxidation resistance or not, that ratio is called Pilling Bedworth Ratio. It's basically a sort of qualitative approach in order to understand the oxidation resistance of a particular metal or alloy this ratio is, it's basically termed as R and this is the ratio between the molar volume of metal oxide and molar volume of metal, but here one thing is to be taken care of, that is this W small w means the weight of metal which is getting oxidized and this capital W is the weight of oxide, so small w is molecular, is basically the molecular weight of metal which is getting oxidized, and small d is specific density of metal, similarly capital W is the molecular weight of oxide and that time we have to be careful that if one mole we have to always consider one mole of metal which is getting oxidized.

Now depending on the situation whether one mole is giving half a mole oxide or one mole is giving one mole oxide this molecular weight of oxide is to be divided by a particular factor. Actually it says that when one mole of oxide is going, one mole of metal is getting oxidized, what would be the volume of oxide that would be forming. And this capital D is specific density of oxide.

Now in order to understand how the factor would be decided there should be a factor which would be coming in this particular ratio while we consider oxidation of one mole of metal, now for example if the reaction is of this sort that means this is 3/2, if the reaction is of this sort that means one mole of metal is getting oxidized and forming M2 or 3 and that is nothing but the half a mole of oxide that is forming. Now in that case this half factor would come here it is to be multiplied with this particular, it should be multiplied by half because 1 mole of oxide is giving half a mole of, one mole of metal is giving half a mole of oxide. Now if the reaction is of this nature that time one mole is giving one mole of oxide there the multiplication factor would be one, so in order to understand it better let us calculate some value, value of R for few oxides, let us consider AL2O3, AL2O3 the reaction nature would be of this kind so that means here Al+ 3 by 2 O2 it would form 1/2 L2O3, now that case if we know the value of capital W of AL2O3 from the atomic weight of all the elements and as well as how many atoms are there in the particular molecule one mole of molecule that time one mole of oxide we can determine the W becomes 101.96 gram and we can also determine the density of this oxide, density of the oxide is 3.89 gram per CC.

Now again we can determine what is the small w? Small w is 26.98 gram and small d is 2.7 gram per centimeter cube. Now if we put all the values and with the factor half so this R becomes 101.96 / 2 x 3.89 and 26.98/2.7 and this ratio becomes 1.308 and the reported value is around 1.28, so it's almost close to that, so this we can make it 1.3, so this value and this value the reported value as well as the calculated value is coming same. And then let us find out one more oxide let's say chromium oxide chromium plus again the reaction would be of this nature. same like AL2O3, the calculation mode would be same and here also we need to put the factor two half, half is to be multiplied with this particular ratio in order to get R, so here also we can find out that W, capital W of oxide is 152 gram, capital D is 5.210 gram centimeter cube, and this density can also be found out by simply considering the density of chromium and oxygen and then having the atomic ratio the way they are mixed, we can also find out this value, this value would be close to this. So then small w would be 52, and small d is 7.14 that time this R would be 1/2 x 152 / 5.210, 52/7.14 this would become 2.0029 and the reported value, reported R is 1.99 which is close to 2, so that means these are the examples, two examples with respect to the first equation. And let us also find out one R value with respect to the second type of equation, where let us find out here, let us find out for FEO, Fe + 1/2 O2 FEO, so W FEO is 55.85 + 16, 16 is the atomic weight of oxygen 55.58 is that the atomic weight of iron divided by 5.745 which is the density of FEO. And then this R equal to this, this is basically the W of FEO and this is the density of FEO. And then for FEO is basically the weight of iron, one mole of iron is 55.85 and the iron density is 7.86 and this would become 1.76 and the reported value is 1.77, so it's coming close.

Now what it means that when 1 mole of atom, 1 mole of metal is going to getting oxidized and forming metal oxide, if the molar volume of metal oxide is more than it is going to cover up the entire surface, and now if it is less it is not going to cover up the entire surface so we can have some exposed area of the metal where oxidation can take place, but if it can cover off, if it can cover up the entire surface then we can have a good resistance which is expected provided that the metal oxide is not evaporating any type, for example in case of vanadium the V2O5 that is the oxide that forms in case of vanadium that V2O5 evaporates, so when it evaporates that time it cannot stay with the surface of the metal so it cannot give any oxidation resistance, so to be protective, for the oxide to be protective that means if we have oxide layer so my oxygen has to diffuse through the oxide layer or metal line has to diffuse out through the metal oxide later this has been understood that there would be diffusion of metal ion or oxygen ion through the metal oxide, that’s what the oxidation goes on. So if you have oxide that means it's forming actually the previously there was one understanding that it provides a sort of protective layer where you can cut them, where basically the contact between metal oxide and metal is disrupted, or disturbed so that's where the resistance comes.

Now in order to be protective few things have to be remembered oxide to become protective, few things one is when you have oxide that time the thermal expansion, thermal expansion coefficient of that oxide and metal should be similar, if they are not similar then there would be stress generation in the oxide and oxides are generally brittle in nature, they will crack and expose the metal surface to the oxygen gas.

Now second is this should be non-evaporative, evaporation should not happen, so for example V2O5 it basically evaporates so it cannot give any protection. Now since the reaction most of the oxidation reactions are oxide growth is happening at high temperature, now if the metal object is under tension or is under stress that time there could be possibility of plastic deformation of that oxide, now if that oxide is brittle in nature the oxide can break, so if the oxide can pause it sort of plastic deformation ability it is always good for the oxide to be protected, so plastic deformation ability of oxide, now again this has been understood later, that there will be always diffusion of metal ion as well as oxygen ion through the metal oxide layer so if we can make the oxide to be very stable as well as to be impervious or if they have sort of low diffusion coefficient, low diffusion coefficient of the metal ion species or the oxygen ion species through the oxide then the oxide is generally thought of having a very good protection ability, so we see that these are the common features that oxide should process to have a very good protection ability of that oxide against further oxidation of that metal. So this is roughly about this Piling bedworth ratio, this is a very primitive understanding about the oxidation resistance of metals or alloys. Now later on more detailed explanation about this oxidation process its mechanism those have been studied and understood, let us get into some of the recent understanding of oxidation of metals and alloys.

Now whenever oxidation takes place that time there would be some sequence of events, before getting into the thermodynamic as well as kinetic understanding of oxidation let us see what will be the sequence of events that might occur during oxidation of a particular metal object. The sequence of events during observations, now the first thing which can occur let's say the metal surface is exposed to the oxygen environment, now the first thing that can happen so you have oxygen gas, G means gas so they come into contact with metal surface and they get decomposed and after decomposition, after they get decomposed so they get absorbed on the metal surface, so adsorption of oxygen to the metal surface, so this is my metal surface, this is my metal surface and on which oxygen are basically oxygen atoms are getting absorbed onto the metal surface, this is the first event that can happen.

Now the second event would be, the second event now this this is happening at temperature T, and this is also happening at some particular partial pressure of oxygen, now at the temperature T depending upon the thermodynamic ability of that metal to get oxidized and to form oxides because of the reaction between oxygen and metal if that is satisfied then oxide can form on the metal surface, so this is the after adsorption of oxygen once the thermodynamic condition is reached which will enable that metals to react with the oxygen and form oxide on the metal surface, so oxides are forming let's say the oxide nature is MO or MO2, let's say the oxide nature is MO2, let us consider the oxide nature is MO, so the metal oxide is forming, and now this metal oxide they are forming like islands on the metal surface and they would try to grow in the lateral direction, so that means the second event would be at temperature T if the thermodynamic criteria is met for the formation of metal oxide then metal oxide would form and then this metal oxide would try to grow so the thermodynamic criteria is reached of course the kinetic is to be satisfied in order to form this metal oxide but if you have enough supply of oxygen as well as the partial pressure of oxygen for the formation of oxide is maintained and if it is higher than the partial pressure of oxygen that is needed oxide formation is possible, so thermodynamic criteria maintain by reaching meeting thermodynamic criteria so this is the stage two. And then, this is first, step one, in the case two for the sequence two case one, case two would be oxide formation on the metal surface, and then third one would be these oxide would grow laterally in order to cover up the surface, so lateral growth, and the forth event would be oxygen are still adsorbed on the metal surface, so the oxygen are still adsorbed on the metal surface and since it's happening at high temperature and depending on the diffusion ability of that oxygen atom, adsorbed oxygen atom the oxygen can also diffuse into the metal so oxygen diffusion can also take place, so oxygen diffusion is taking place, so actually the oxygen is getting dissolved in the metal, so we can determine what would be the dissolved amount of oxygen in the metal from the phase diagram of that particular metal oxygen phase diagram and from that we can determine what could be the percentage of dissolved oxygen that can stay in the metal without forming any oxide, so this will be in the lattice, so these are dissolved oxygen.

So fourth stage it is basically dissolved dissolution of oxygen, dissolution of oxygen so this is the second stage of or the second sequence of, set of events that are happening in the second stage. Now in the third stage there would be, see the third stage this oxide is growing this way laterally, now once the metal surface is covered up so let's say the metal surface is covered up this is the metal surface, so this is the metal surface, once the metal surface is covered up by the oxide let’s say this is my oxide layer that has formed on the metal surface, this oxide layer would try to grow in this direction, so this is my metal surface and this is a more oxide layer so after it covers up the entire surface laterally then they would try to grow in the perpendicular direction so the thickness of the metal oxide would increase. Now once we have metal oxide how would they grow? So that is, that growth process would be decided by the diffusion of, by the diffusion of metal ion as well as oxygen ion and the conduction of electron through this oxide layer, so there could be oxygen, this side we have oxygen, so oxygen can come in as the, in the form of oxygen ion and they can come to this surface and react with the metal ion or the metal ion can also diffuse out and then it can come to this surface and then again react with oxygen ion then form metal oxide, and if this event is happening that time electron can go there so now from this picture we can also have some sort of correlation between oxidation and aqueous corrosion.

Now at this point we see that oxygen is diffusing in or metal ion can go out or diffuse out to this metal oxide layer and there could be electron transfer from this surface to this surface, this can give you a sort of, this can be correlated with the aqueous corrosion also, now if you see the aqueous corrosion so we need four things for the corrosion, aqueous corrosion to happen, one is cathode, second is anode, so cathode surface cathodic reaction would happen and anode surface anodic reaction would happen, then third case we have solution which is nothing but electrolyte then we have conductor which actually transfers electron, so these are the four components for aqueous corrosion and if we see that for example if we see that this is my zinc rod and if it is in HCL medium we see that zinc corrosion can take place, so what happens the some places there are places where zinc will go out in the form of zinc ion, and how the zinc ion would be forming, then zinc actually would 2 electrons will be taken out from zinc and then zinc ion would form, and this zinc ion, this two electron would go here, near the place, near around this place so there hydrogen ion would take care of this electron and then form hydrogen, so this is my anodic reaction, this is cathodic and then this electrons are basically transmitting through the conductor which is the zinc rod and electrolyte which is the HCL solution, which is acting as electrolyte through that the ionic conduction is taking place.

Now here if we come to this place let's say the general reaction MO M+ +O - - if these two things react then we can have MO, so that time we have MO formation, and now first M++, in order to form M++ we can have this reaction, two electrons can be taken out from the metal atom and then it will form M++, and these two electrons can go to the oxygen so oxygen can take this two electron and form oxygen ion, now this is anodic reaction and this is reduction or cathodic reaction, so this and this will react, now react and then form MO, now this process can happen on the surface because here we have metal surface, so this reaction is happening at this surface and the anodic reaction happening at this surface, so this is my anode, this is my anode, now once we have two electrons which are excess in the metal these two electrons can transmit through this oxide layer and it can come here, it can come here these two electrons and then oxygen, adsorb oxygen is already there, see the absorb oxygen can take care of this two electron, can take this two electron and then this reduction process can happen can occur on this surface or interface, so this interface is basically nothing but cathode since the cathodic reaction wherever the cathodic reaction occurs that surface is considered to be cathode, so this is my cathode so that means if you compare this process and this process so we have one anode and one cathode, here also this is my anode, this is my cathode, so two electrodes are done, this is my gas, this is my metal oxide, so gas oxide interface is acting as cathode and oxide metal interface, oxide metal interface is acting as anode, so two electrodes are done, so this two electrodes are done so conductor this oxide itself is acting as conductor of electrons so the electron is, if this oxide is conducting electrons which takes the electron from this surface to this surface, so this is also done, this is done, this is done, and this is also acting as electrolyte where we have, in this case this process if you consider so here we have, if these process is happening on this surface so on this surface we have oxygen ion and then metal ion can go through this oxide layer and whenever, and that means this is acting as a solution just like in aqueous corrosion where the ion movement is possible, so this ion movement is taking place through this oxide so this oxide is also acting as electrolyte. So all the four steps are there, so this is acting as electrolyte as well as conductor, so if metal ion goes from this end to this end so metal ion will react with oxygen and the oxide growth would take place on this surface and if oxygen ion there could be possibility of oxygen ion which can diffuse in and the metal ion will stay here, so oxidation that time oxidation would happen on this surface, so this process is when oxygen and diffusion in, oxygen diffuses in, and this is the case where metal ion diffuses out, so this is the overall similarity between the oxidation process, oxidation process and aqueous corrosion almost similar, because all the four components are also there in the case of oxidation. So we see that there are resemblance between oxidation process and aqueous corrosion.

Now we were discussing the stage 3 where we see that oxide film is forming and that oxide film is growing gradually, and then we have oxygen and metal ion diffusion and the conduction of electron those events are also happening, now at the same time there would be continuing dissolution process oxygen still would dissolve into the metal, now this process would go on and finally in the stage 4 we can have a defect formation in the oxide layer because the continuous growth of, due to the continuous growth of oxygen oxide and due to this diffusion process, diffusion process.

Now the stage 4 we can have different generation, this is metal surface, this is metal surface oxygen diffusion is still taking place with a continuation of oxidation, now this metal oxide, now there could be cavity formation, this is my oxide layer, this is my oxide layer so this is one cavity, so this is one cavity, this is one cavity that can form, and here if we can, there could be a development of small crack like this, so there could be development of small crack like this so oxygen can, the gaseous oxygen can go in through this cavity, there could be formation of pores in the oxide layer, let's say this is my pores, this is my pore, this is cavity, this are pore, even we can have micro cracks, this is micro crack, micro crack formation, and of course the other events the previous events are also taking place continuously.

Now this is the stage four and then this is basically the different generation, defect formation, and in the stage five this oxide layer this is metal, this is metal oxide, there could be a formation of macro crack like this, this is the formation of macro crack, this is my oxide layer and this is my metal surface, this is my metal surface, so oxide layer and these are the macro cracks as well as cavity, of course there would be porous, there could be pore formation, more pore formation, so like this the events are going on, as well as the oxide layer is also going on, oxide layer is also, the thickness of the oxide layer is also increasing and as well as the oxygen diffusion is also taking place, so dissolution of oxygen is also taking place. Now at this stage there could be other events for example even in the beginning, from the beginning of the process there could be evaporation of oxide or there could be possibility of embrittlement of the metal, embrittlement of metal due to oxidation, and this oxidation could be internal oxidation. Now this oxygen which is diffusing in and that oxygen sometime the diffusion would be so fast maybe if the oxygen is diffusing in through the grain boundaries which are generally the open space region so that case the internal oxidation can also take place, and then that would, that might lead to embrittlement effect of the metal, so these are basically the series of events which are forming, which are happening, which are taking place sequentially.

Now this is when a metal, these are basically the steps or events which can happen during the metal oxidation, now let us see what one reaction to another reaction that are possible, one reaction we have seen that the metal is basically, metal is reacting with oxygen this is forming metal oxide or this is half or there could be this oxidation can be possible due to the presence of H20 the vapor phase as well as the presence of CO2 so metal which can also get oxidized, in the presence of water vapor, so this is MO + H2 if we would like to have a general balance then we can put it like this XM YH2O and then we can have MXOY and then Y H2 so then the general balance is done and also we can also have oxidation of metal due to the presence of CO2 again this is my general balance so MX OY + Y CO so this many reactions that could be possible during oxidation either due to the presence of oxygen gas or due to the presence of water vapor or CO2, so these are the common reactions which are encountered during oxidation of metal.

Now let us discuss the thermodynamic understanding of oxidation, so thermodynamics whenever we talk about thermodynamics of any event we basically consider the possibility of that process or event. Now if let's say any process Del G which is the free energy change at constant pressure and time if it is negative less than 0, we can say that the process is possible, so possible reaction or reaction, or event, or process. Now this particular concept would be considered while considering the thermodynamics of oxidation, now whenever we have particular reaction let's say M + O2 it's forming MO so that means we can balance it like this, so now in this process this is let's say the solid phase, this is gas, this is let's say the solid again, the oxide which is forming that is solid, now this process is happening at a particular temperature T and let's say it's also happening when the atmospheric pressure is 1, now that time we can determine the free energy change for this oxidation process and the free energy change for this oxidation process we can determine from the reaction isotherm we have already talked about this reaction isotherm which says that this is equal to - RT LN K, so this is my overall reaction isotherm and this process this case the equilibrium constant in the non-standard condition, now this reaction if it is not at equilibrium at that temperature T then the free energy criteria can be written in this way. Now if it reaches equilibrium then we can also see the expression for K which is basically MO 2 or let us, let me write it in that form of activity and partial pressure of oxygen, so activity of MO and activity of M and partial pressure of oxygen, now if we put it here then it would become Del G0 and if we consider these two phases, the pure metal and pure metal is getting oxidized and forming the pure oxide and that time since they are pure we can consider their activity to be 1, so then K would be equal to 1/PO2, so we can replace this K, RT Ln K and then we can say that this is 1 / PO2, I think I made a mistake here, it should be plus the reaction isotherm so this is if we replace the non-standard K with this equilibrium constant with partial pressure of oxygen then the free energy change for this or forward process is becoming Del G0 - RT Ln PO2.

Now if the process reaches this reaction, reaches equilibrium then this goes to 0 when at equilibrium, so that time my Del G0 is coming out to be RT Ln PO2, so for oxidation and this is nothing but the standard free energy change for oxide formation and when the pressure is one atmosphere so this and this free energy change which is the standard free energy change at temperature T, since the temperature is T here, and when the pressure is one atmosphere, that is the definition of standard condition that the pressure will always be one atmosphere. And then once we know this, this will give you the idea whether oxide formation would be possible or not, now for the oxide formation we should see that whether this condition is met or not. Now let's say the oxygen partial pressure, oxygen partial pressure which is the equilibrium partial pressure let's say, equilibrium partial pressure which is determined from this, from this equation once we get the value of Del G0 at temperature T, the equilibrium partial pressure at a particular temperature T if it is less than the actual partial pressure that the metal is exposed to PO2 actual, then what would happen? Let us see whether we have this condition or not, now if we see that, now we have to start with this equation Del G this equation from this equation we have to start and when we start from this equation we can easily determine whether the oxidation is possible or not from the initial condition what we have, what has been written on this side.

Now if del G is considered, Del G0 + RT Ln PO2 and this would be the actual and this case we can replace it with RT Ln Po2 equilibrium, so this equation is becoming RT Ln PO2 equilibrium + RT Ln PO2 actual, now if this is more than this value, so what would happen? So this would become positive, so if the equilibrium partial pressure of oxygen at particular temperature T is less than the actual oxygen partial pressure that is existing on the metal surface then we can determine what would be the free energy change, now if we consider this equation - RT Ln PO2 this is actual and this part we can replace it with RT Ln PO2 equilibrium, now since PO2 actual is greater than PO2 equilibrium so this part always would be more than this part, so this is then RT Ln PO2 actual would be greater than RT Ln P O2 equilibrium so then this term would be negative, so or less than 0, that means this condition is met, so the reaction is possible, so oxidation is possible, so oxidation is possible.

Now similarly if we see that this is greater than this or this is greater than this that time the things will reverse, so this would be positive, greater than 0 and then oxidation second stage oxidation is not possible, so depending on the oxygen partial pressure and its effect on the total free energy change this Del G whether it's negative or positive that would decide whether the metal would oxidize or not oxidize at that particular temperature with the existing condition of partial pressure of oxygen.

Acknowledgement
Ministry of Human Resource and Development

Prof. Phalguni Gupta
Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

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Jai Singh
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Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
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Light & Sound
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Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

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Ajay Kanaujia
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Direction
Sanjay Pal

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an IIT Kanpur Production