

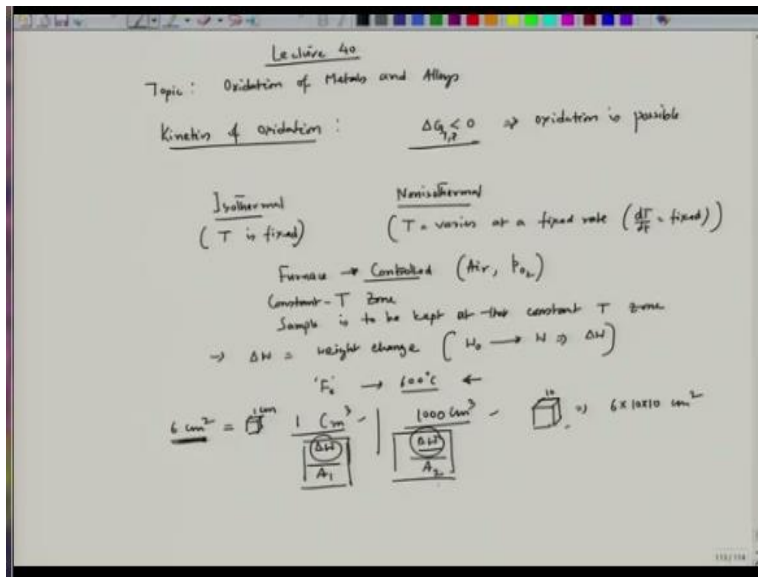
Corrosion - Part II
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Lecture - 40
Kinetics of Oxidation

Hello everyone, so we have our lecture 40, till now we have been talking about thermodynamics of oxidation. And our consideration was oxidation of a metal in presence of oxygen only forming metal oxide which is stoichiometric and metal is also pure it is a closed system. And the system would like to reach equilibrium at a particular temperature and that equilibrium is dictated by is given by partial pressure of oxygen.

And from that we could draw Ellingham diagram and as well as we could see that how oxygen scale is generated which are actually radiating lines from $\Delta G^0 T$ at 0 say at T is it is equal to 0 at 0 Kelvin which indicates partial pressure of oxygen to be 1 atmosphere. And so those facts we have understood from our earlier lectures and now we will talk about kinetics of oxidation.

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Now lecture 40, so topic oxidation of metals alloys and now we will discuss kinetic. So we could see that when delta G less than 0 TP is then oxidation is possible. But whether what will be the rate of that oxidation we have to also understand that because that rate will tell us what is the

degree of oxidation. Now in order to find the rate without understanding much of the mechanism of oxidation, I mean to say how oxidation takes place.

Like in a metal oxidation can be decided by movement of metal ion from inner surface to outer surface. And this inner surface is nothing but the metal and metal oxide interface and outer surface is nothing but oxygen and metal oxide interface. So this could be one possibility, there could be possibility that metal oxygen ion can move from oxide oxygen interface to the metal oxide interface.

So and also there could be possibility that metal ion as well as oxygen ion they are reacting at the in inside not at these 2 extreme interfaces rather they are forming inside the metal oxide. So all those possibilities are there which need more detailed analysis of the structure of oxide. But without looking at that part one can easily find out kinetics of oxidation from by doing a simple experiment.

So when we talk about kinetics it has been noticed that kinetic process has got a different rate loss. Like the oxidation process can be linear it can be parabolic, it can be logarithmic, it can be cubic and those processes those rate loss are specific to some metals of course there are reasons for it. But at least we can find out whether this particular oxide formation is parabolic or not or cubic or not or something like that.

So in order to do that we need to do experiments there are 2 ways one can find out. One is isothermal another one is non isothermal, so these are the 2 routes. So isothermal as the name suggest temperature is fixed but here temperature varies at a fixed rate, that means dT is fixed. So we will not talk about non isothermal because the treatment for non isothermal is bit complex but isothermal treatment is fairly easy.

Now for that you need a furnace which should be controlled furnace it can be done in air or a particular partial pressure of oxygen can be maintained and there should be a constant temperature zone in the furnace and the sample is to be kept at that constant temperature zone, fine. And now

we will measure what are the measurement parameter ΔW is the weight change from the initial weight let's say initial is W_0 .

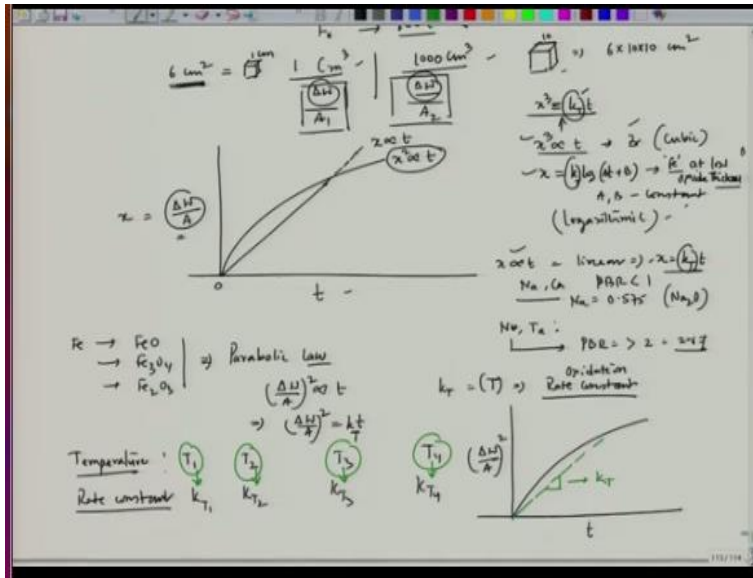
And then the weight change after oxidation is W , so then it becomes weight change because ΔW , since the oxidation is basically reaction between metal with oxygen at the surface. So now in order to avoid differential areas of the same sample exposed to a particular temperature and having difference in weight gain. For example, if I try to measure oxidation of iron at a particular temperature let's say 600 degree Celsius and all the other conditions are fixed.

But in one case I am using 1 centimeter let's say one case I am using 1 centimeter cube sample, another same case I am using 100 centimeter cube sample. So that means in both the cases if I only measure ΔW I will have erroneous data. Because in this case ΔW would be much higher and if and at the same time if they are the same sample, same temperature all the other parameters are fixed then they it should have the same kinetics.

So if that means it should have the similar level of weight gain with some normalize factor because here we are using different areas this is basically the volume of that particular cube this is the volume of that particular cube. If we take a different volume if this is a cube of 100 centimeter cube and this is 1 centimeter cube of course in this case let's say if I take 1000, so the length is 1 side is 10.

So that means the total area becomes and in this case length is 1 centimeter cube, so it total length 6 centimeter square. So surface area exposed to the oxygen in this case would be much higher, so ΔW would be much higher in this case. So in order to avoid this area factor we have to divide it by the initial area, so which will normalize it with respect to these 2 difference in area, so this is A_1 , this is A_2 . And then we should get at the same level of this parameter for a particular time interval and what we plot.

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We plot time as a function of ΔW area and then since this is 0 point so 0 point it can be like this which is this is in this case if this parameter is considered to be x . So x proportional to t it could be x square proportional to t or it could be cube or it could be logarithmic. So I am just considering these 2 cases and our interest would be this one because many of the cases we see that parabolic rate law is followed except few cases like in case of zirconium we see that cubic law is valid where x cube is proportional to t .

So in case of zirconium or at a low thickness of oxide x we can also have a logarithmic scale which is indicated by

$$x \propto \log (At + B)$$

Where A and B are constants. So this is valid for a system for example in case of iron it will be experience and a low oxide thickness we experience this kind of rate loss this is cubic, this is logarithmic, fine, so these are the possibilities.

Now we can see that linear that means this linear law is possible for sodium or calcium where I could see that PBR ratio is less than 1. For example, in case of sodium this PBR ratio is 0.575 where oxide is nothing but Na_2O . So then when it is PBR ratio is less than 1 that means the surface is not covered with oxide. So I have easy access of oxygen with the metal, so even this particular linear law is possible in case of niobium or tantalum.

So there for example in case of niobium PBR ratio is more than 2 which is close to around 2.67, so that means since PBR ratio is very high. So there could be possibility of crack formation on the surface and once the crack forms that metal surface is expose to oxygen and then linear law can be experienced. And but in case of iron if the temperature is more than 540 degree Celsius ok.

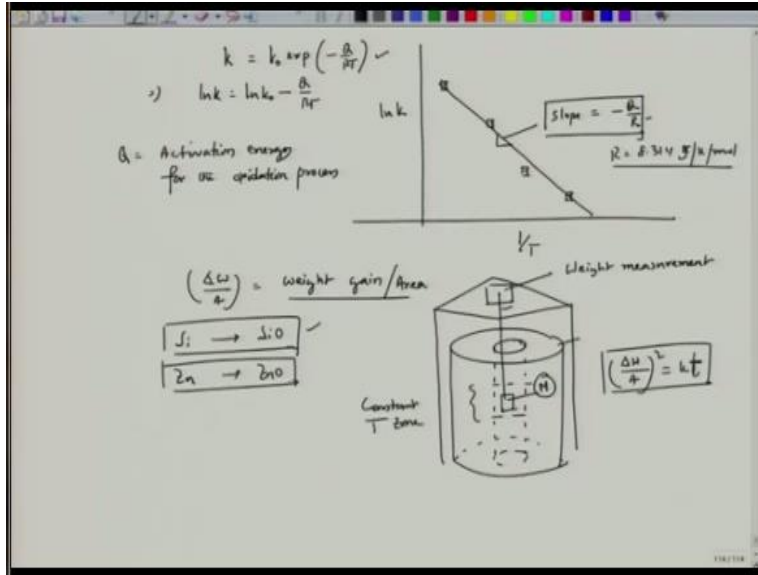
So before we talk about iron I could see that whenever we are drawing this parameter why we are calling isothermal because we are doing temperature is fixed and these parameter is measured with respect to time and that is what it is called isothermal oxidation experiment. Now we could see that there is a cubic law, there is logarithmic rate law, there is a linear rate law and in case of iron oxide iron to iron oxide or to Fe_3O_4 or it can be going to Fe_2O_3 there I could see we can see that parabolic rate law is valid.

So where $(\Delta W/A)^2 \propto t$, I can write is kt , so this is at a particular temperature. So I can see that kt is specific to our temperature which is a rate constant, so this oxidation rate constant. And in those cases also I can write this one as $x = k_T t$ which is this becomes rate constant for a linear rate law. Here also I can write it as $x^3 = k_T t$, so this is also rate constant.

Here also I can write instead of a proportionality I can write $k t$, so this becomes my logarithmic rate constant. So here it is parabolic rate constant. Now I can do at 4 temperatures T_1 , T_2 , T_3 and T_4 I can measure this is let's say temperature, this is a rate constant same experiment I will repeat at different temperatures. So I can find out rate constant as a k_{T_1} , k_{T_2} , k_{T_3} , k_{T_4} , how so I will do, this parameter with temperature I will see that parabolic law will be valid.

Now I can after that I can take a square of it and then if I plot square of that with temperature I should get a straight line and that straight line the slope becomes k_T ok that way I will do for the same all those temperatures I can get corresponding rate constant.

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So once I get this rate constant I can use this very Arrhenius equation

$$k = k_0 \exp\left(-\frac{Q}{RT}\right)$$

So I will plot, so now I can write this

$$\ln k = \ln k_0 - \frac{Q}{RT}$$

So I can plot $\ln k$, $(1/T)$ at 4 temperatures I will get this 4 data points. And then I can do a linear approximation and after doing that I will get the slope which will be nothing but Q by R . So R we know R is nothing but 8.314 joule per Kelvin per mole.

So once we know this I can find out Q is nothing but the activation energy for the oxidation process, fine. So now we could see that without understanding much of mechanism of the process at least I could get useful data for the isothermal treatment isothermal oxidation operation at what are those useful data one is at a different temperature what is the rate constant oxidation rate constant and once we know rate constant had couple up more and at least 4 temperatures.

We can do this kind of treatment and get the activation energy for that oxidation process, now interestingly here we have talked about weight change. Now this weight change is bit tricky you have to be careful while seeing this weight change most of the oxides we see weight gain ok. But and that time it will be ΔW that times ΔW by A is nothing but weight gain per unit area, fine but there are metals at some high temperature.

For example, silicon if it forms silicon oxide or if it is zinc if it forms zinc oxide, so those cases I might see that the instead of weight gain I could say weight loss. Because these are oxides with a high vapor pressure, so they could evaporate. So instead of having weight gain I can get weight loss since we are measuring the weight of that particular metal with the help of a weighing machine previously it used to be done crudely you know tube furnace you can design your furnace.

You have a tube furnace like this let's say you have a tube furnace you have stand then keep a weighing machine, weight measurement and then hang a sample like this. So this is let's say the metal where you want to do the what oxidation behavior of that particular metal you want to study you put on the furnace first ok. And then see the constant temperature zone let's say this is my constant temperature zone hang the sample to this particular zone.

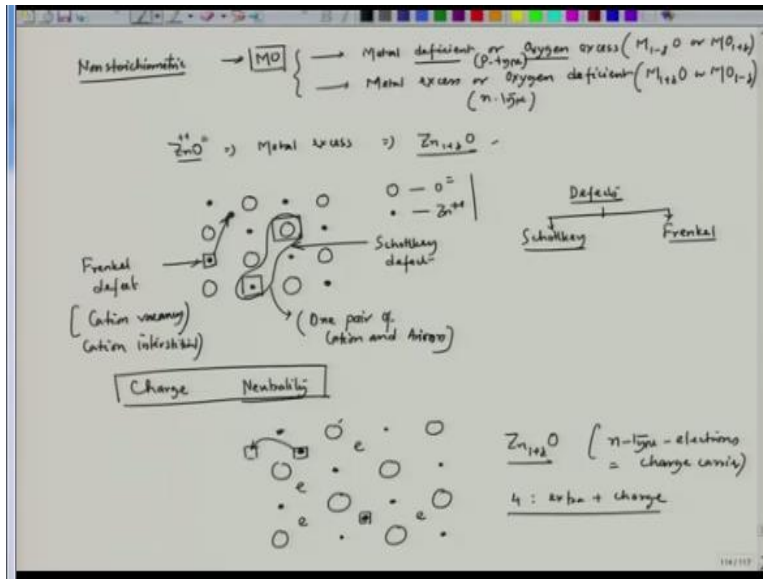
Of course this metal wear with what you will be using should be having sufficiently large of high oxidation resistance that what that metal weight measurement it should not that oxidation of that particular wear should not come into your data. So you are seeing the weight gain and that you are measuring with respect to with time, so that will give you the weight gain data as a function of time.

Then you know what is the initial area of that particular sample you just divide that particular initial area for all the weight gain data and plot weight gain by area that particular information with time and you then see whether it is follows linear plot or parabolic plot. So in order to do that what you have to do, you have to again plot $\Delta W/A$ with reference to T and see whether it is falling linear or you can plot $(\Delta W/A)^2$ and then plot with respect to time and see whether it becomes straight line.

Because if it is a parabolic then it should be equal to kt , so this will be a straight line, so that should be a straight line. So if it is a straight line then of course it is a parabolic rate law and then you can get the information and all the cases we are saying weight gain. But in this case at least silicon oxide if it forms then it should not be weight again rather it should be weight loss ok.

So this is about the kinetics of the oxidation without knowing much of mechanism of it one can find out kinetics like this. But our interest is to see the mechanism part ok, so in order to may know the mechanism part one has to understand structure of oxide.

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So in order to know the mechanism of oxidation we need to know a bit of structure part of oxide till now we have considered oxides are stoichiometric. But it is not like that. Oxides are generally non stoichiometric that means if I take an oxide MO it can be either metal deficient or oxygen excess or it can be metal excess or oxygen deficient, now both the cases I can write this.

For example, in this particular case I can write it since I am considering that this one to be non stoichiometric. This one I can write it as $M_{1-\delta}O$ or $MO_{1+\delta}$ and delta is a very small quantity and this is of course fraction, here I can write $M_{1+\delta}O$ or $MO_{1-\delta}$ ok. So these are the 2 rotations we can use to indicate non stoichiometry in case of metal oxide like MO, now whenever we have such situation if it is a metal deficient oxide.

Then or oxygen excess then will have a particular kind of oxide, where the charge carrier will be a positive hole we call it positive hole that time it is called p type semiconductor and when it is metal excess or oxygen deficient that time the charge will be carried by electron that time it is called n type semiconductor. So these are the 2 situations we can come across and once we have these 2 situations.

Then we would see that in both the cases whether it is a p type or n type the diffusing species either could be metal ion or oxygen ion depending on our typical situations what we have. For example, if I consider zinc oxide which is a metal excess oxide I can term it as zinc $1 + \delta$ O, so if I try to do a simple very simple arrangement of these cations and anions. Because here we have cations and anions, so I can put cations to be a small dot, anions to be a big circle.

Because anion has greater size in this particular case, so now I can have this arrangement like this, fine, so this is a kind of arrangement where this is - zinc ++ and this is a stoichiometric situation. Now in oxide there could be defects and interestingly defect free material is not possible because of the entropy considerations you can look into a standard textbook to understand why this entropy consideration rather mixing entropy consideration does not allow any material to reach to a perfectly pure condition ok.

So that is what every material has got defect and in case of oxides also we have defects, so defects are in the form of either defects can be either common defects either Schottky this is one defect and then another defect is Frenkel. So these are the 2 defects that are possible in oxides, fine, so these defects are appearing because if I consider Schottky, for example this particular situation if it is a Schottky defect then 1 anion and 1 cation these pair will be vacant.

So that time it becomes Schottky defect this is also definitely point defect because this 2 lattice points are missing. And in case of Frenkel one of the sites let's say this site it is left vacant and this particular cation will move to the interstitial. So this is interstitial, so this region is interstitial, so this becomes, so now that time it forms Frenkel defect, that time it becomes Frenkel defect.

So now in one case in case of Frenkel, I create anion in this particular case cation vacancy and in this case I am having and cation vacancy of course in parallel we are creating cation interstitial, fine. But in this case 1 pair of anion are missing from their usual sites, so these are the 2 defects that are possible and of course these 2 defects will decide finally which species will try to diffuse through and another important aspect in this oxide.

We have to maintain neutrality and when you talk about neutrality I am talking about charge neutrality. So this is to be maintained in the oxide and accordingly we will have a different situation depending on whether it is a metal deficient or metal excess or oxygen excess or oxygen deficient different types of defects as well as missing sites we can generate as well as we can have difference in their charge carrying mode.

In one case I will have positive holes to carry the charge and in another case electron will carry the charge. So now in this case at least for zinc oxide we can explain that in case of zinc oxide I will see that particular situation again ok. So now in this case if it is $Zn_{1+\delta}O$ where δ is a very small quantity that means we have 1 extra zinc ion and here we see that these are the notation for zinc ion and oxygen and these are oxygen this is zinc.

So we have 1 extra zinc which is sitting let's say 2 extra zinc are there, so this 2 are extra zinc ion that are there. Now once we have 2 extra zinc ion then of course I could see that it has 4 extra positive charge, now if there are 4 extra positive charge that means then we have to have 4 electrons in the system in order to neutralize this 4 extra positive charges. So that is what we have 4 electrons ok, so this is the structure we get.

Now that means in this case and that is why it is called n type why because here electron becomes my charge carrier and of course we have interstitial position is filled with that excess zinc ion. So this interstitial position can exchange because here we have 1 interstitial position it can exchange through this and that way zinc ion will move through the oxide layer. So this is that means the diffusion through this interstitial diffusion and the charge carrier would be electron.

So this is a kind of n type oxide, so like that we can also explain other oxides whether it is a p type or n type, so let me stop over here and we will actually we will have one more extra lecture in order to understand this aspect. So it will be total 41 lectures rather than 40 lectures, so today at least we stop here, we will continue for one more day, thank you very much.