Indian Institute of Technology Kanpur

NP-TEL
National Programme
On
Technology Enhanced Learning

Course Title

Environmental Degradation of Materials

Lecture – 39
Broad Subject: Oxide structure and Oxidation

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Defect structure of metals and alloys oxide and its oxidation will be discussed, so defect structure of metal oxide and oxidation. Now whenever we see a metal is getting oxidized, so this is metal side, this is let's say MO, where the stoichiometry is 1:1 and then you have oxygen environment, so this is oxide environment interface and this is metal oxide interface. We see that the simplistic approach in order to understand how the oxidation is taking place and this is already discussed while discussing the similarity between oxidation and electrochemical corrosion phenomena, so we have M releasing 2 electron going to M2+ which is anodic reaction, so this is anode, and now this one diffuses through the metal oxide and reaches through this oxide environment interface and at the same time this 2 electron will also reach to the other end and that means oxide is acting as conductor because it is also transmitting electron from one end to the other end, and these two electron oxygen adsorbed oxygen will accept this 2 electrons which is basically a reduction process and go to oxygen 2 minus and this is reduction so this is cathodic side, which is cathode? This interface is cathode, so now this one will react with M++ and then form metal oxide. So we see this oxide it also will act as electrolyte since we are saying that the ion transmission from one end to another end is taking place through the metal oxide, so it is acting as conductor as well as electrolyte.

Now we are in this case oxide growth will take place on this end but if other way around if we see that this one transmits through this oxide layer and comes here and then here 2++ O - reacts and then form MO so the oxide growth will take place on this end so that means whenever we see that metal ion goes to the anode surface to the cathode surface that time oxide growth is taking place on this end that means on the oxide environment interface and if oxygen is coming here and then on the metal oxide interface oxide growth is taking place. Now there could be a simple experiment which can tell you that which is the governing factor or which interface is actually growing and also we see that and that process is called platinum, that is called a kind of noble metal attaching a noble metal wear before the oxidation on the metal surface and seeing the position of that noble metal wear on the oxide surface after oxidation rather. So that is basically the marker experiment, so if we do marker experiment, so that case let's say this is the metal surface this surface is getting oxidized this surface, and on this surface let's say we put some platinum wear marker, this is platinum wear marker and then we are exposing it to oxidation and seeing that what would be the position of this marker after oxidation, so then we can see two situation, one is let's say if this is metal and this case this is metal and these are markers which are platinum markers, which are platinum wear, now let's say after oxidation we see that the platinum wear is basically on top of this oxide layer and now this is MO and this is O2 gas, if the platinum marker on top of the oxide, outside this platinum markers is based are basically on the outside of the surface which is getting oxidized, then we can tell that the oxidation growth is taking place on this surface, oxidation growth is taking place on this surface, that means this is happening due to inward diffusion of oxygen.

Now similarly if we see on the same diagram, if we see that so another case would be if we consider that this is the other surface, the inside surface and if we see that those platinum wears are basically on the inside surface this is the platinum wear position, this is another position, this is another position, so we have the platinum wear actually its position, wears are on the inside surface of the, inside surface after oxidation and that means this is on the surface between metal and metal oxide that time the second case, this is first case, second case the oxidation growth is taking place on this end, oxidation growth is taking place on this end. Now that means this is generally happened, this is happening because of metal cation are diffusing outward, outward means metal, metal oxide to metal oxygen interface, so the position of this marker we can clearly tell that where the oxidation is actually oxide, where the oxide is actually growing. Now this marker experiment would definitely depend on the reactivity of the marker with the metal oxide or metal and because this reaction, this process is generally taking place at higher temperature as well as thickness of this or the diameter of the wear. Now if the diameter of the wear is more than the thickness of the oxide layer then it would not give any indication that where the oxide growth is taking place, now from this marker experiment it is very clear that there is a diffusion of oxygen anion or metal cation through the oxide layer and the diffusion is due to the defect structure of the metal oxide.

Now let us see what are the defect oxides, defects in the metal oxide? Defects in metal oxide, so generally we see that in solid we have four types of defects so we have four types of defects, one is point defect, an example of point defect is vacancy or interstitial atom or in case of oxide it would be cation or anion in case of oxide. Then we have line defect, one example of line defect is dislocation. Then we have surface defect, example of surface defect green boundary or any surface and of course there could be a volume defect, example of volume defect could be void, so we have four kinds of defects in solid. Now our primary interest would be the point defect in oxides, so let us discuss what are the point defects, common point defects which are important for our current discussion? So let us discuss point defect in oxides, and before coming to the point defects we know that the point defect is thermodynamically stable consideration and the amount of point defect that exists in a particular solid that would be determined from this formula - Del HV RT where this is a burger true number and this is number of point defect this is the molar energy for formation of that point defect, R is gas constant and T is basically the temperature in Kelvin, so from this we can determine what is the percentage of or the fraction of point defect that exists in a particular solid, in the oxide also this formula is well valid.

Now in most of the oxides they are generally ionic in nature, so now if we consider ionic oxide that means they have cation site and they have anion site, so but one particular consideration in case of ionic oxide there we always see that the sum of charge cationic charges would be equal to sum of anionic charges and of course it will maintain electroneutrality so the electroneutrality would be maintained.

Now in case of oxide we can divide the defects in make oxides we can divide them into, or the point defects in oxide we can divide into two segments, one is stoichiometry defect and then we have non-stoichiometric defect but they are in stoichiometry defect there are two major defects one is schottky and another one is frenkel defect. Now in case of non-stoichiometric defect we have many varieties out of that we would only consider two major varieties and those will lead to, one is P type defects, P type oxide, the another one is N type oxide, and P type for the charge carrier is basically the hole and in N type charge carrier is electron.

So now let us see what is schottky and frenkel and also what is stoichiometric defect, in case of stoichiometric defect generally the anion and cation concentration are maintained constant, so stoichiometry means let's say one metal oxide is denoted like this MO and where cation and anion ratio is 1:1 and this will always maintain 1:1 so this is called stoichiometry in oxide or it is stoichiometric oxide. Now in this case we have schottky defect, schottky defect for example if we have anion, let’s say the negative is anion, and there is a small one positive which is cation so like that we can have distribution like this, then we have like that we can, let's say this is a simplistic form of that oxide lattice, now where we have let me extend it by one more layer like this so we see that there's a small part of that particular oxide where we have the same number of cation and same number of anion so I think in order to make it same 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, so ten 10s so the total electro neutrality is maintained and the schottky defect, in that case 1 anion would be missing, 1 cation would be missing, cation from its normal lattice point site it would be missing, and 1 anion would be missing, so if we remove this 2, remove this 2 that means there would be a cation vacancy and there would be 1 anion vacancy and that creates the schottky defect so that means this is my defect, so the defect is basically you have a vacancy of cation, let's say the cation is denoted as X and vacancy of, sorry anion is denoted as X and cation is denoted as M so you have vacancy of cations, same number of cation and same number of anion both are missing from their normal lattice points. And so the overall MO and in this case actually MO is maintained, now if this is double, double charges so if we have double charges there, so even if we miss one and one there, one cation and another anion so overall this 1:1 stoichiometry is maintained at the same time you see that overall electroneutrality is also maintained, this is schottky effect that means the equivalent amount of metal cation and anion are missing, now this is schottky defect then we have frenkel defect, in case of frenkel defect there and let us come to the same diagram if we consider frenkel now we put all those points back again all those cation and anion now that case since cationic size is smaller than anionic size so then there could be a vacancy which is created here and then that cation will come and sit here in the interstices, so this is basically this cation has moved to the interstitial position which is basically the interstitial position of all four atoms, four ions and it's basically a vacant site, so this is my frenkel defect. So if in case of frenkel defect no cation and anions are missing actually the missing site the cation which is basically missing from the normal lattice site that cation will go and sit in the interstitial position and then it will give you frenkel different.

Now coming to the non-stoichiometric defect and before we come to the non-stoichiometric defect let me tell you, this stoichiometric defects, stoichiometry is very hard to found, hard to be found because thermodynamically they are unstable so in order to explain the oxidation behavior of metal we need to concentrate more on non-stoichiometric defects, so non-stoichiometric defect so one could be P type, so the P type defects are basically either it could be metal excess where X is anion and M is cation in the lattice, so this is metal excess or there could be oxygen deficient oxides 1, 2 – delta, so this is M X2 - delta so they form N type oxide, so that one example is, for example if we consider this one that time the example is zinc oxide or it could be this one where we have ZnO2 this is another one example, this is zirconium oxide.

Now let us see the defect structure of ZnO, now if we consider the defect structure of ZnO then we can have a small part of the lattice in two dimension so Zn++ O - - so like that we can have distribution, if we consider this and since we have the common formula with Zn 1 + delta O so that means there would be excess cation, so excess cation let's say there are two excess cation and those will be in the interstitial position so here is one and here is one, so these are the two excess cation. Now if we have two excess cation then in order to maintain electroneutrality there will be excess electron, four excess electron this is a basically a simplistic approach and this would be sufficient for our understanding on the oxidation behavior of zinc oxide so these are two cations in the interstitial position and there will be four electrons which will neutralize the entire system and this here the charge carriers those electrons, so the charge carrier in this case electrons and that's what this is called N type, and then if we try to find out the diffusing species for the oxidation, here the diffusing species is the interstitial Zn++ which will half and then this will come to this position, this will come to like that this will try to move and if we consider this is metal surface and this is oxygen surface then this way the diffusion would take place, so the interstitial movement of atoms, interstitial movement of those cations would be the diffusion control step and the charge carrier is basically the electrons and this is N type oxide.

And another stoichiometric defect which is P type and there we can also have the demonstration of P type oxide, in case of P type oxide either we have metal deficient and this is cation, this is metal or we can have oxygen excess or a anion excess so 2 + delta, one example is uranium oxide and this example is Nickel O, NIO, FEO like that but those are the oxides which have P type structure, so in this case the charge carrier or charge carrier is hole, electron hole and diffusion is happening through the movement of metal ion vacancy, so how does it happen? Let us see that, so that case we have Ni O, Ni++ O - -, Ni++, O - -, so let me draw the full structure, so this is O, this is also system simplistic representation of this oxide in two dimension.

And now we see here the oxide non-stoichiometry like this Ni 1 - delta O, so that means there would be missing nickel cation sites, so if we have two missing cation sites so that means two vacancies are created, now in order to, so that means we have two extract anions in the system, two external negative charges in the system so in order to balance those two extra rather four extra negative charges that means these two Nickel ion, here we have one nickel cation, here another nickel cation both two nickel cations are missing, that means four negative charges would be extra so in order to neutralize those four negative charges there would be a hole creation this is hole so that means nickel in the normal site would ionize and ionize and form the hole so there would be four hole, four hole, this is one, two, three, four, so the four holes are created so it's a balanced, so this is here the charge carrier is electron hole and diffusion is basically by through this vacant cationic site. So this is the P type oxide which is nickel oxide or iron oxide. Now once we know this two types of oxides then we can also explain in case of P type as well as N type how the oxidation is taking place, let us try to understand that so the oxidation mode in P type and N type, let's say we consider oxidation of metal excess oxide so zinc oxide where we have excess metal cation in the interstitial position, so there if we see the somatic representation so this is oxide, and this is zinc, this is O2 and there we have anodic reaction on this surface which is metal oxide surface metal oxide interface, metal oxide interface there we have anodic reaction, and then this two electron will go through, electronic conduction will happen and then this electron will go to the other side and then oxygen will accept 2 electron and convert to oxygen 2 - which is cathodic reaction, and this metal cation will again diffuse through the metal oxide layer by the mechanism of interstitial diffusion and it will reach to this surface and then these two will react and form metal oxide, so your oxidation growth is taking place on this surface so this is in case of oxide with excess cation or N type oxide, now there could be also a possibility of N type oxide with oxygen deficiency so it could be Zn, let's say MO 1 - delta so there we have oxygen deficiency we can also have a sort of ionic movement as well as electron transfer and we can also explain how the oxidation is taking place, but there we have oxygen vacancies so that diffusion would be or the oxygen anion to this surface so in this case we have oxygen vacancies so that means if we have oxygen vacancies that oxygen vacancies will try to, now this is the second case where you have less oxygen in the lattice so you have oxygen vacancies, so the oxygen vacancies, through the oxygen vacancies we have anion movement or the diffusion on to this surface, to this section this will go this way, oxygen vacancy will go this way and on that way oxygen anion will come this way so oxygen anion will come to this surface, but rest of the thing would be same and here oxygen anion will react with 2+ because there is no cation interstitial only the anion vacancy, so the anion vacancy will move to this side and anion will move to this surface so here the reaction would happen that means cation and anion will react and form MO, so the second case the oxidation growth will take place on this surface, so this is the explanation of oxidation in case of N type oxides where either you can have excess metal in the interstitial position or oxygen vacancy.

So let us also look at what happens in case of P type oxide, and we see in case of N type oxide that oxide growth would be at two different interfaces depending on whether it's metal excess N type oxide or oxygen deficient, N type oxide and in case of P type oxide let us consider metal, sorry in case of N type metal excess oxide or oxygen deficient but in case of P type let us see what happens in case of metal deficient P type oxide, so if we see the metal deficient P type oxide how the growth is taking place, so we can have another two different interfaces, let me draw it in, this is metal, this is metal oxide and this is oxygen, now same thing this side anodic reaction would happen, now since this is, this kind of oxide so we have vacancies, cationic vacancies so this will base into, this metal cations which are forming due to anodic reaction at this interface would try to diffuse through the oxide by the interchange of, by the collective diffusion of metal vacancies, so the metal cation vacancies are also moving this way and due to this process this is diffusing from this interface to that interface. Now this two electrons will come here and these electron would move to the other end and here oxygen will accept two electron and then form oxygen anion and by the time you have presence of metal cation on this interface so this two will react and form MO so the metal oxide growth would be at this interface, but this electron transfer which is taking place here is not what we have seen in case of N type oxide, the electron transfer is taking place by exchange of electrons via the electron hole, through the electron hole, how the exchange of electron through the electron hole that is taking place? Let us see that process, now here we have two electrons which are coming through the metal to the other section, now if we consider here what happens metal and also we have hole here, so hole will try to move this way and electron will try to move this way, so now there will be hole and electron interaction so we have hole which is nothing but M+++, this is actually hole +E which will form M+2 so that means due to this interaction, hole and electron interaction which is basically the trivalent metal cation reacting with electron and forming M2+, now again this M2+ so electron has come from this to this point, now again M2+ will, one electron will be removed from M2+ so another hole will be formed, so this will form another hole so and this hole will also again react with electron and form M2+ again and then this will again one electron will be again taken out so this part is, if we consider only that this part so again it will form hole and we have seen the hole is nothing but metal cation, so we see that electron is moving from this end to the other end due to the interaction with hole and the reaction nature is like this so there would be always exchange like this, so there would be always like this, so due to this exchange electron is moving from this end to the another end due to the exchange, due to the interaction between hole and electron, and so finally we have electron reaching there, so this electron is actually on this surface and gradually we have more and more electrons which are coming at this surface which will form, which will favor this reaction which is cathodic reaction, so the oxide growth is taking place here.

Now we see that the hole is also moving this way there could be a possibility and this metal cation diffusion is taking place through the hole metal cation interaction and this hole, couple of holes they can combine, they can combine and they can form a pour here, so this is pour, so one pour can be created due to the interaction or combination of many holes and this is the mechanism how the pour forms in P type oxide. So this is one example how the oxide growth is taking place, in case of P type oxide where we have metal cation deficiency and also we have seen in case of N type how the oxide growth is taking place.

Now let us come to since we have seen the oxide structure in case of P type which is nickel oxide or in case of N type which is zinc oxide so if we dope them with a cation, with less valency than the metal cation in the normal lattice point, all replacing the normal lattice point cation with another cation which has more valency than the cation which is being replaced, so what would happen in case of, what would happen to the oxidation of that kind of that metal. Now let us first come to zinc oxide, in case of zinc oxide we see that the oxide structure is like this, let us replace one of the zinc cation from the normal lattice point with a lithium cation, another one let us replace with lithium cation and we can also replace one more cation with lithium plus, so that means we are replacing 3 zinc cations with monovalent, lithium cations, now that case what would be the nature of this structure? So now that case we see that if we have 3 lithium cations which are replacing 3 zinc cations so we see that there would be 3 excess negative ions, now that case in order to balance that 3 excess negative ions, negative charges not ions, negative charges then if we increase one interstitial cation then we see that there is one more negative charge which is to be neutralized, so in order to neutralize that one more negative charge we can get rid of one extra electron so we see that now this is neutralized so that entire oxide is neutral so that case we see that number of cation interstices are increases, so cation interstitials are increasing, number of cation interstitials is increasing so we have five cation interstitials, previously it was 4 cation interstitials and 3 extra electrons, so the charge carriers concentration is decreasing but the interstitial atom cation concentration is increasing, and the diffusion is taking place by the movement of this interstitial cation through the interstitial positions so that means if we increase, if we replace zinc cation with lithium cation then we have increase diffusion species, so if we have increased diffusion species of course there is a decrease in charge carriers but the diffusion is basically taking place via this interstitial diffusion, so if we have increased diffusing species so there would be more oxidation, so if we replace Zn++ with Li+ we have increase in diffusion species that means increase in cation interstitial we have more oxidation that means oxidation resistance would decrease.

Now let's the situation be like this, let the situation be like this zinc cation, so 3 zinc cation is replaced by 3 aluminum cations so that means we have 3 extra positive charges, so that case in order to balance that 3 extra positive charges we can, if we increase the electron contained, so if we make it 5 electrons so that means we balance so that time this would be replaced by Al++, so that case if we make 5 electrons, so that means we see that 2 extra positive charges are remaining which are to be balanced, so now if we remove 2 zinc positive charges so then we see that we have left with 1, we are left with 1 zinc cation in the interstitial position, so that means in this case and then you see that overall balance is done, now that case we see that in this case we see that total number of diffusing species decreasing and hence oxidation resistance would increase, so that means if we dope zinc with zinc oxide with aluminum then we see that there is improvement in oxidation resistance, but if we dope zinc oxide with lithium plus then the oxidation resistance will go down. Now what would happen in case of nickel case? So in case of nickel if we replace 3 nickel cations from their normal lattice points with Li+ now that case we see that total number of negative charges, so we are replacing Ni++ 3 with 3 Li+ so we say that 3 extra negative charges are there in this lattice, now if we replace one vacancy with Ni++ then we are left with one negative charge, extra negative charge and that extra negative charge can be balanced by forming one extra positive hole so then you see that the overall neutrality is maintained, charge neutrality is maintained.

Now in this structure we see that the vacancy concentration is decreasing, vacancy concentration is decreasing that means if we decrease this vacancy concentration there would be less Ni++ diffusion through the oxide layer and if there is less Ni++ diffusion then my oxidation resistance would increase. Now the situation let's say I replace 3 Ni++ with 3 Cr+++ so that case instead of lithium we put chromium, and then one more place is here, so that means here we have 3 extra positive charge so in order to balance that 3 extra positive charge we can create there could be creation of more vacancies so we can create 1 more extra vacancies this was, this could be 1 more vacancy, so we have 3 vacancies, so if we have 3 vacancies then 1 extra positive charge is still left, so there could be, left with 1 extra vacancy, so 1 extra positive charge and in order to balance that we can reduce the positive hole, so if we reduce positive hole we see that overall balance is maintained, neutrality is maintained and that case, in this case we increase this is first case, and the second case vacancy concentration increases, and if the vacancy concentration increases that means diffusion of Ni++ would be faster, and if it is faster than oxidation would be faster, so resistance would go down, so oxidation resistance would go down, but generally we see that the chromium addition is for improving the oxidation resistance of iron, that is true if the chromium content is beyond certain critical limit.

Now in case of doping in order to have this benefit of doping, in order to have increased oxidation resistance we need to dope it maximum up to 5%, but if it is beyond 5% situation would be different. For example in case of chromium addition, in FEO or iron so there if chromium contained is beyond 18% so instead of FEO layer there could be a formation of CR2O3 layer, and if the CR2O3 layer forms on the surface then it could have, it could give a very good oxidation resistance rather there is a decrease in oxidation resistance, so the chromium oxide layer would form and that concentration is about 18% chromium in iron so that case chromium oxide would form on the surface and on iron surface and it could give a very high oxidation resistance.

Acknowledgement
Ministry of Human Resource and Development

Prof. Phalguni Gupta
Co-ordinator, NPTEL IIT Kanpur

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

Camera
Ram Chandra
Dilip Tripathi
Padam Shukla
Manoj Shrivastava
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Editing
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Badal Pradhan
Tapobrata Das
Shubham Rawat
Shikha Gupta
Pradeep Kumar
K.K Mishra
Jai Singh
Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan

Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

Light & Sound
Sharwan
Hari Ram

Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

Production Manager
Bharat Lal

an IIT Kanpur Production