Corrosion -Part II
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Lecture - 41
Oxide Structure and Oxidation Mechanism

Hello everyone, today we will have the last lecture and this lecture is basically a kind of supplementary lecture in order to complete the concept what we started doing or understanding in lecture 40.

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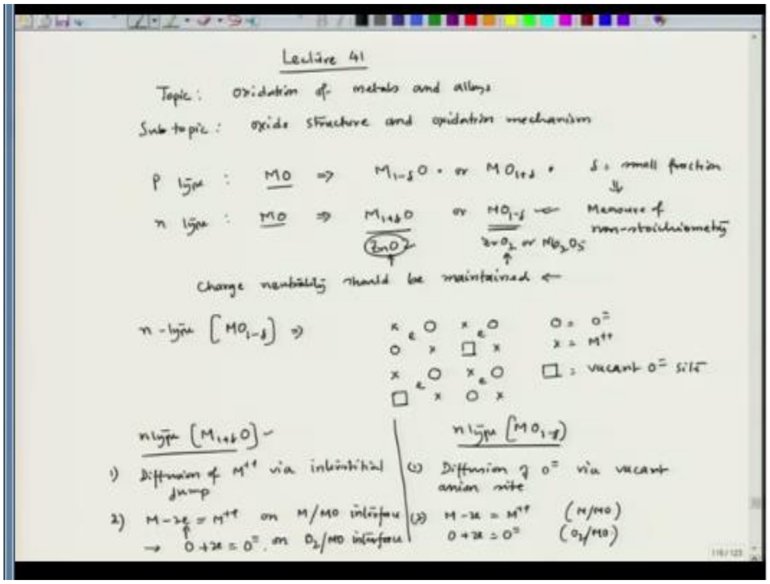

Lecture 41

Topic: oxidation of metals and alloys

Sub topic: oxide structure and oxidation mechanism

p type : MO ⇒ $M_{1-\delta}O$ or $MO_{1+\delta}$ — δ = small fraction ⇓ Measure of non-stoichiometry

n type : MO ⇒ $M_{1+\delta}O$ (ZnO) or $MO_{1-\delta}$ (ZrO_2 or Nb_2O_5)

Charge neutrality should be maintained ←

n-type $[MO_{1-\delta}]$ ⇒

○ = $O^=$
× = M^{++}
□ = vacant $O^=$ site

n type $[M_{1+\delta}O]$

1) Diffusion of M^{++} via interstitial jump
2) $M - 2e = M^{++}$ on M/MO interface
→ $O + 2e = O^=$ on O_2/MO interface

n type $[MO_{1-\delta}]$

(1) Diffusion of $O^=$ via vacant anion site
(2) $M - 2e = M^{++}$ (M/MO)
$O + 2e = O^=$ (O_2/MO)

So this is lecture 41 and we will discuss the main topic would be of course same as the previous one which is oxidation of metals and alloys. But mainly we are considering metals pure metals and the sub topic for today is oxide structure and oxidation mechanism. In the last lecture we ended our discussion on the structure analysis of zinc oxide. And we saw that there could be 2 types of oxides one is p type or n type and out of p type there could be 2 situations.

One situation could be a metal deficient oxide or oxygen excess oxide, in case of n type either it could be metal excess oxide or oxygen deficient oxide. So there could be 2 oxides one is p type another one is n type and in the p type there could be 2 situation one is for example if this is the metal oxide it could be $M_{1-\delta}$ O or $MO_{1+\delta}$ and δ is a small fraction which actually is nothing but the measure of deviation from stoichiometry.

Since the stoichiometry of this oxide is 1:1 but once you have this 2 situations one is this another one is this you are actually deviating from stoichiometry, n type there could be 2 situation for example again this is MO which is n type oxide let's say. So then it could be either $M_{1+\delta}$ O or $MO_{1-\delta}$. This 2 situation can be possible and where again delta is nothing but the small fraction which is nothing but the measure of non-stoichiometry.

Now out of that we started discussing about $M_{1+\delta}$ O which is a n type oxide one classic example is zinc oxide. And in this oxide we could see that zinc cation which is the extra that is present in the oxide lattice goes to interstitial and because you have extra metal cation in order to fulfill the neutrality or the charge neutrality of the oxide. So the concept is nothing but the charge neutrality should be maintained whether it is metal deficient or metal excess or oxygen deficient or oxygen excess that oxide should be neutral.

And in order to maintain that neutral in case of zinc oxide we could see that there would be excess electron. So in that situation electron would be the charge carrier and that is what it is called n type and interstitial zinc cation they can exchange sites with the nearby vacant interstitial site and then the diffusion of metal ion would take place. So now we will first try to understand n type case 2 cases and one example for this could be Zirconium oxide or niobium oxide.

So those are oxygen deficient oxide and also n type, so let's see how the oxidation process happens in case of oxides with metal deficient diffusion of interstitial cation. Now we can have 2 situations one is this another one is this since we have understood the structure nature of zinc oxide let's understand if the situation is like this. So now n type with $MO_{1-\delta}$ this situation this is a kind of imaginary oxide that is what we will take up for our understanding.

So we can have a kind of structure like this, so for example this cross is metal cation and circle is oxygen anion, so if the distribution is like this. So now if I see a simplistic approach, so here we have this is oxygen anion, this is metal cation and this is the vacant oxygen cation site. So here we have 2 vacant cation site, so that means we have 4 extra positive charges, so we have to neutralize that 4 extra positive charges.

So there will be electron generation, so these electrons are the charge carrier, so it becomes n type. But here you have oxygen vacancy from the normal lattice sites, so the diffusion would be through the vacant anion sites. So if I try to compare these 2 situations one is n type where $M_{1+\delta}$ O that situation, another situation is n type where $MO_{1-\delta}$ this situation. So in this case we have if we go back to the last part of lecture 40 you would understand that why there should be interstitial cation in this situation.

So now first case is a diffusion of M++ via interstitial jump, now in this case diffusion of oxygen ion via vacant anion sites. So this is the difference between the diffusion of species, now in this case the anodic reaction happens which is M - 2e = M^{++} it happens on M/MO interface. And here and of course these electron goes to the other side of the interface that means oxygen oxide interface and there we have O + 2e = O^{2-} on oxygen metal oxide interface.

So these 2 reactions happens this is anodic reaction this is cathodic reaction they happen on the 2 interfaces. But here also this remains same metal 2 electron it moves to it goes to M^{++} and this happens on M/MO interface whereas + 2 electron go to 2 - on oxygen metal oxide interface.

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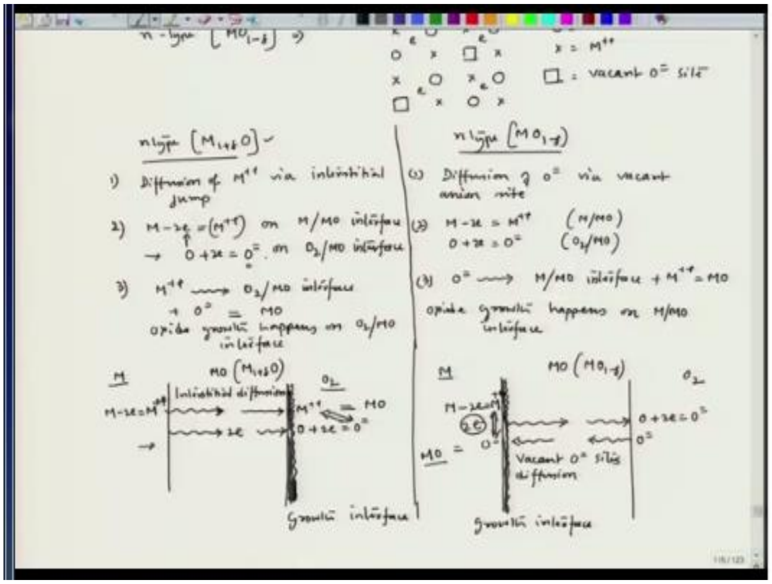

n-type $[MO_{1-\delta}]$ ⇒

x = M^{++}

□ : vacant $O^{=}$ site

n type $[M_{1+\delta}O]$ ✓

1) Diffusion of M^{++} via interstitial jump

2) $M - 2e = (M^{++})$ on M/MO interface

→ $O + 2e = O^{=}$ on O_2/MO interface

3) $M^{++} \rightsquigarrow O_2$/MO interface + $O^{=}$ = MO

oxide growth happens on O_2/MO interface

n type $[MO_{1-\delta})$

(1) Diffusion of $O^{=}$ via vacant anion site

(2) $M - 2e = M^{++}$ (M/MO)

$O + 2e = O^{=}$ (O_2/MO)

(3) $O^{=} \rightsquigarrow$ M/MO interface + M^{++} = MO

oxide growth happens on M/MO interface

So there is a similarity but in this case metal ion moves to the other end and then reacts with O^{2-}. So third is metal ion migrates to oxygen metal oxide interface and then combines with O^{2-} which becomes MO, whereas in this case oxygen ion migrates to M/MO interface and then combines with M^{+2} form MO. So now here the oxide growth happens on oxygen metal oxide interface, whereas here oxide growth happens on interface, fine.

This is the 2 distinct scenarios we can arrive at, so let's see how we can graphically show that. For example, in this case let's say this is my oxide layer which is MO and of course this is nothing but $M_{1+\delta}$ O. So M - 2 e = M^{++}, it migrates via diffusion, since there are metal ion cation interstitial and that interstitial can exchange position with another vacant interstitial by its site and since there is a overall gradient of metal ion on this side.

So that is what the metal ion will try to migrate or diffuse from metal-metal oxide interface to the oxygen interface oxygen metal oxide interface. And of course these electrons will also move to the other end, where it reacts with oxygen combines with oxygen and form oxygen 2 - and since this metal ion goes to this side. So this 2 will combine and form metal oxide, so the oxide growth happens on the surface ok.

So this is a typical mechanism what we have here and now on the other side this is the growth interface, now in the case where you have oxygen deficient n type oxide. So there you have this is again the oxide layer which is nothing but $M_{1-\delta}$ this is M, this is oxygen. Now here metal loses and then form + + which stays here because we don't have any missing sites or metal or cation interstitial.

Now here we have this electron 2 electron this will migrate to the surface and then combine with oxygen 2 -, this oxygen 2 - will migrate from metal oxide oxygen interface to the metal metal oxide interface via the vacant oxygen cation sites diffusion. So now this oxygen will ion cation will come here and then they will combine and form a metal oxide. So that means here the growth happens on this interface the oxide growth happens on this interface.

So this is growth interface this is the typical difference between the oxygen mechanism in these 2 situations both are n types but one case you have metal ion cation interstitial another case you have oxygen vacant sites oxygen cation vacant sites.

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Now let's see the situation in case of p type, p type case we have 2 situations, one is $M_{1-\delta}$ O and second is $MO_{1+\delta}$. These are the 2 situations we can come across, now if I try to see their structure, so this classic example of this one is iron oxide or nickel oxide. So which can be written as $Fe_{1-\delta}O$ or $Ni_{1-\delta}O$, so these are the metal deficient metal ion deficient oxide.

So if I see the structure let's draw a simple model which is let's say this is cross is metal ion and circle is oxygen anion. So this will be the distribution, so now we have deficient metal oxide metal ion cation, so let's put a vacant cation then we have, so now here X + + - - so this are the nomenclature. And now this is vacant cation site, so now since we have 2 cations missing, so we have extra 4 negative charges because of this excess oxygen that is present in the lattice.

Now in order to neutralize, this cation would try to leave 1 electron and then form X + since X is considered to be M+++. So X + is nothing but M+++ which is typically bivalent metal cation with 1 electron hole. So here also since there should be 4 such situation, so now we have 4 electron holes which are nothing but the extra positive charge in order to neutralize excess negative charge due to extra cations present in the lattice.

So for example if it is nickel, so the structure would be Ni+++, so this will be the situation what you can experience. In case of iron also you can have this typical situation. Now here the situation is little different because we have extra and now this particular situation can arise in case of uranium oxide where cation is very large, anion is very small. So now if this is my cation that is what I have drawn little bigger size X, so this is anion.

So now X cation with reference to of course this we are not taking the actual picture what we have in case of uranium oxide. But we are just taking hypothetical oxide with $MO_{1+\delta}$ and this is which is nothing but anion or and this is M++ with reference to this. Now in this case we have extra anion, so they will be in the interstitial position, so now let me put it in this fashion these are interstitial, so this is anion interstitial.

So now we see that there are 4 extra negative charges, so that is what they will have 1 electron hole 4 electron hole should be present. So this X+ is nothing but M+++, so this is basically we call it hole, fine. So now you see both the cases the charges that charge is transferred via positive hole and diffusion would be different here. In this case diffusion is via the cation diffusion through the vacant cation sites but here diffusion of oxygen via interstitial oxygen diffusion or the interstitial anion diffusion. So now if I try to see the mechanism in this situation just the way we have done for n type.

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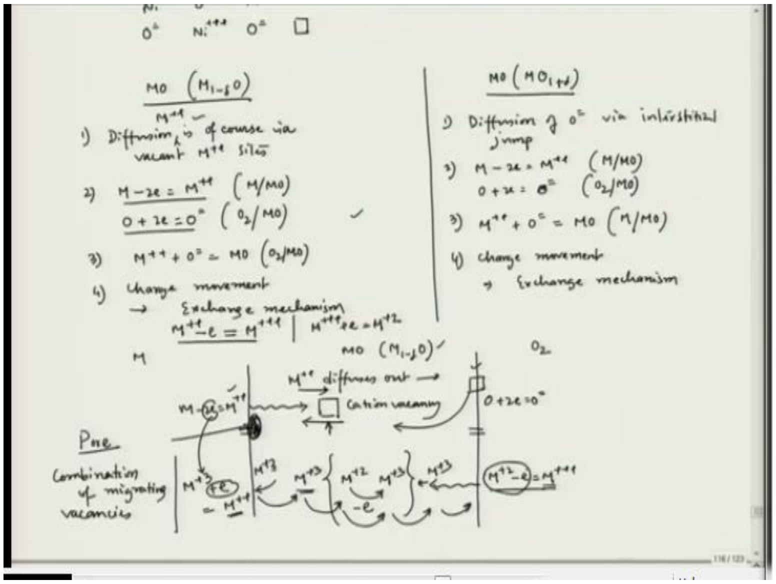

So here it is MO with $M_{1-\delta}$ O this is a p type with cation vacancy, so now if I try to see 1 the diffusion is of course via vacant cation sites. And here the diffusion should be metal ion that will be diffusing, second part this reaction which is anodic reaction would happen on metal metal oxide interface, third is metal oxide and of course the other corresponding reaction

$$O + 2e = O^{2-}$$

That would happen on oxide metal oxide interface.

Now this is the cathodic reaction, this is anodic reaction, now we have to see which way which species would migrate since we have seen that this metal oxide metal cation would migrate from inner surface to the outer surface that means metal-metal oxide interface to the oxygen metal oxide interface. So that means the combination reaction would happen on oxygen-metal oxide interface, now you have to see how the charge would move.

Now in this case the charge movement happens via exchange mechanism which is nothing but M + 2 and M + 3. So like that it will move or you can also make it like this

$$M^{+++} + e = M^{++}$$

So like that way the charge would move, now this is the case for metal deficient but for the metal oxide where $MO_{1+\delta}$ which is the p type. So that case diffusion of O2 which is the anion via interstitial jump metal this will be happening on MO sites M MO sites, this will MO site.

So these interfaces they will happen, now oxygen is diffusing to the combination reaction between metal cation and oxygen anion forming MO that would happen on MO interface and the charge transfer movement will be via exchange mechanism. So now if I try to see graphically what happens here, now if I see the 2 interfaces this is oxygen, this is metal oxide, this is metal of course this is $M_{1-\delta}$ O. Now

$$M - 2e = M^{++}$$

and here

$$O + 2e = O^{2-}$$

These 2 reactions are taking place.

Now metal ion should move to the other end because we have metal cation vacancy diffuses out. And now we have to see the charge how this charge is transferring from this end to this end. So we have to see the charge transfer since this is metal deficient oxide, so the deficiency happens where there is a combination of metal ion and oxygen ion. So that happens here, so here we are generating electron hole or

$$M^{2+} - e = M^{+++}$$

that is forming.

So this + 3 is exchanged in this fashion, so this is M+2 and here M+3, so electron goes to this, so then it becomes like this. So this particular reaction is taking place, so now here M + 3 is coming up, so now we are generating vacancy this electron hole here or we simply say that hole. So that is coming because of this and now whenever we have this particular reaction then M+3 is moving to this end.

So and then again there is another exchange of electron, so M+3 is coming here, so finally it comes to this interface this M+3. So M+3 combines with and when electron it forms M++ and these electron this electron combination is coming from this. So this 2 electro which is being released by metal that combines with M+3 and forming M++. So now this way M++ going to M+3 and leaving M+3 and then again this mechanism is going on, so finally here M+3 is combining with electron and forming M+2.

So that way the mechanism of oxidation happens in case of p type oxide, of course in the p type oxide of course this when metal deficiency is there. Now interesting part is this cation vacancy which is generated here because it is forming non stoichiometric oxide these vacancy is migrating through from this end to the other end. So this vacancy movement is this way and metal ion movement is this way.

So the vacancies are coming this metal sites cation sites which are vacant those coming on the other end gradually. Now if those vacancies for example number of vacancies they combine each other, so that time there could be possibility of pore generation. So let's say this is a pore who it generates due to combination of migrating vacancy, fine, so there could be porosity formation on the metal-metal oxide interface.

So this is the mechanism what could be possible in p type. Now let's not continue any further from this. There is a great effect of this metallic metal oxide structure and that can decide how do we alloy them. So that we can introduce resistance to oxidation, for example if we take n type and for example zinc oxide if we add a kind of metallic iron which has lower vacancy than the metal cation present in the usual lattice then that would reduce the concentration of interstitial and also decreases the excess electrons.

So now if it should be lower vacancy and now if that lower valancy metallic ions for example lithium ion if we impregnate in zinc oxide then it reduces the zinc oxide cationic sites this interstitial sites. So once we reduce the zinc cation sites in the interstitial position, then of course there will be reduction in oxidation rate because the growth will be because the zinc cation will no more move diffuse as faster as possible in the situation where there were large number of zinc + + interstitial sites.

So that would reduce the oxidation rate but again if we add aluminium which has higher valancy + 3 compared to the zinc which is + 2 that case again zinc cationic sites this zinc zinc ion concentration in the interstitial position would increase and that would again lead to increase in the oxidation rates. Similarly, if we consider p type oxides let's say metal deficient oxide, nickel oxide or iron oxide.

There if we add lower valancy cations which is like a doping then the concentration of cation vacancy would decrease and increase the electron holes. And of course because the concentration of cation vacancy is reducing and that would lead to decrease in diffusion rate of metal cation. And hence oxidation rate would decrease but it happens just reverse if we add if we just dope a metal cation with a higher valancy than the iron let's say.

So there for example chromium. Then chromium has got + 3 whereas iron has got nickel has got + 2, so that time metal cation sites vacant sites would increase and of course that would decrease the electron hole concentration. So since we are increasing the metal cation sites the metal cation vacancy sites, so that would increase the rate at which the metal cation will move from metal-metal oxide interface to the oxygen metal oxide interface.

So oxidation rate would increase, now interestingly this chromium when you added at a very small content to nickel oxide or iron the oxidation rate increases. But if we have extra chromium then that chromium forms make on chromium oxide and then it will protect the metal part from oxidation. So but we are not getting into the protection part or the effect of alloying on the oxidation rate. So because that will be taken up in the next stage of next corrosion course which will be corrosion part 3.

Now if we try to see what we have taken up in this particular course, we have started with corrosion and we have analyzed different corrosion phenomena or corrosion events with the help of mixed potential theory. And this mixed potential theory also comes in cathodic and anodic protection and that is what we have also considered cathodic and anodic protection and analyzed it from the mixed potential theory.

And then gradually we move to oxidation and in the oxidation we understood we try to understand thermodynamics and kinetics of oxidation and also the mechanism of oxidation however we have to now get to the protection part. Now in the corrosion part 3 we will be taking up protection of metals and alloys in case of corrosion there could be protection due to alloying, there could be protection due to micro structural change, there could be protection due to working condition.

And then there could be protection due to environmental change or going for coatings, going for inhibitors. So those are the factors will be taken up in corrosion part 3 and from the oxidation site will take up effect of alloy that means once we go for alloying that means we are talking about the oxidation of alloys how it changes just like the what explanation that little bit of hint has been given that if we add dope elements with different valances in a metal oxide that would lead to change in oxidation rate either it can reduce or increase the oxidation rate.

And then there could be coatings, for example sterlite coatings, there could be boron oxide coating, those coatings can also help in reducing oxidation rate of metals and alloys. So for the time being we will end here and we will learn more in the next level of course which is the corrosion part 3. So till then thank you very much.