Corrosion-Part II
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Lecture-36
Pilling Bedworth Ratio of different Metal Oxides

Hello everyone, today we will have lecture 36.

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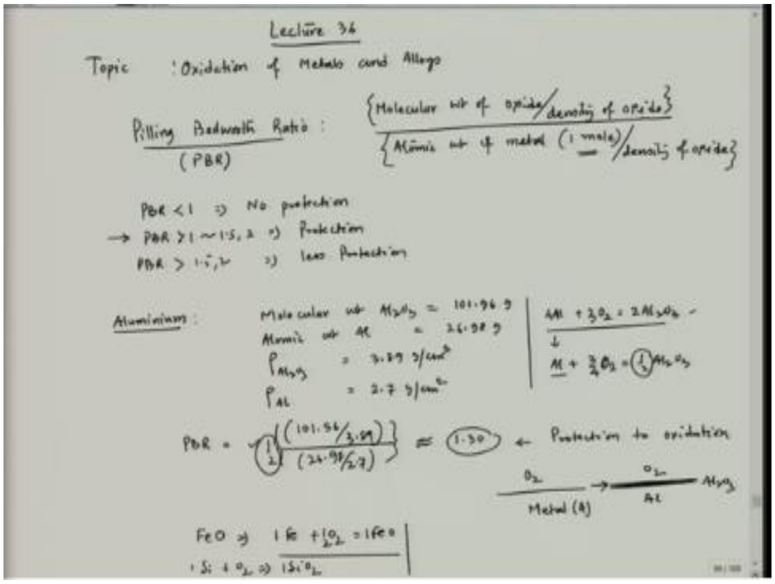

Lecture 36

Topic : Oxidation of Metals and Alloys

Pilling Bedworth Ratio (PBR) : $\frac{\{\text{Molecular wt of oxide}/\text{density of oxide}\}}{\{\text{Atomic wt of metal (1 mole)}/\text{density of oxide}\}}$

PBR < 1 ⇒ No protection

→ PBR > 1 ~ 1.5, 2 ⇒ Protection

PBR > 1.5, 2 ⇒ less Protection

Aluminium :

Molecular wt Al_2O_3 = 101.96 g

Atomic wt Al = 26.98 g

$\rho_{Al_2O_3}$ = 3.95 g/cm³

ρ_{Al} = 2.7 g/cm³

$4Al + 3O_2 = 2Al_2O_3$

↓

$Al + \frac{3}{4}O_2 = \textcircled{\tfrac{1}{2}} Al_2O_3$

$PBR = \frac{\textcircled{\tfrac{1}{2}}\{(101.96/3.95)\}}{(26.98/2.7)} \approx \textcircled{1.30}$ ← Protection to oxidation

FeO ⇒ $1Fe + \frac{1}{2}O_2 = 1FeO$

$1Si + O_2 \Rightarrow 1SiO_2$

And we will continue our discussion on, so the topic is oxidation of metals and alloys. In the last lecture what we have seen different stages of oxidation of a metal when the metal is in contact with oxygen at a high temperature. And we have seen them mainly there are 5 stages are starting with adsorption of oxygen followed by nucleation of oxide on the surface as well as dissolution of oxygen in the form of solid solution or liquid solution in the metal.

The solid solution or liquid solution I mean to say when the metal is in solid state then it is solid solution, when it is liquid state it is a liquid solution of metal and oxygen. And this dissolution of oxygen in the form of solid solution or liquid solution that could lead to internal oxidation and then we have a film of oxide on top of metal and that film can generate cracks, that could be micro cracks or macro cracks even there could be porosity and there could be also spallation that means the oxide can spill off spall off from the surface of the metal.

Because oxides can have a different thermal expansion coefficient as well as there could be problem of a differential volume change. And when we started talking about differential volume change we talked about Pilling–Bedworth ratio. And this ratio is designed on the basis of whether the metal oxide that forms on the metal surface covers the entire surface or not.

If it covers then we would say that it provides protection to accept further oxidation, and if it does not then it will not give protection. But in the case where it covers if it is too much of oxide volume from the oxidation of 1 mole of metal. Then that case there could be a possibility of fracture of metal oxide which might lead to formation of macro cracks or micro cracks or even spallation of oxide from the surface leading to exposure of metal surface to the oxygen again.

So that case it will not be able to provide much of oxidation resistance, so if we talk about pilling Bedworth ratio. So we this is a ratio between molecular weight oxide divided by density oxide and that is to be divided by atomic weight of metal of 1 mole, this is very important. And now we will do some numerical problem and there it will be clear that why this 1 mole is important divided by density of oxide and there we and this shortly is called as PBR.

Now we also notice that if PBR is less than 1, no protection PBR greater than 1 but 1.5 to 2 it gives protection and PBR greater than 1.5 or 2 then less protection. In all those 3 cases if we notice carefully that only it considers that what is the volume of oxide that generates because of oxidation of 1 mole of metal. But it does not consider several other things which are very very important we will see one by one and few examples classic examples we will see.

Now at least if we go by this PBR let's do some calculations let's do a calculation for aluminum. In case of aluminum molecular weight of Al2O3 = 10196 gram, atomic weight of aluminum 26.98 gram, Rho the density of Al2O3 = 3.89 gram per centimeter cube and density of aluminum 2.7 gram per centimeter cube. Now since we are considering that here it will when aluminum is oxidized it forms Al2O3, so we have to write the chemical this reaction

$$2Al + 3O_2 = Al_2O_3$$

So this is the balanced equation, now if we see that we have to consider 1 mole of metal which is getting oxidized. So if we convert it into 1 mole, so it would be, so now we have to consider molecular weight and density of the oxide of half mole of Al2O3 since 1 mole of metal aluminum gives rise to half a mole of Al2O3. Now interestingly if you see this particular thing these are indicating the volume of the metal of 1 mole.

And here it is the volume of oxide which is generating from 1 mole of metal oxidation. So if we try to calculate PBR it will be = 10196/89, so this will be 1.30 around 1.30. So if we see this particular value this particular value lies in this range, so we can say that it gives you protection to oxidation. And in fact Al2O3 is a very good example which gives a very good protection to aluminum since it forms a thin layer on top of aluminum.

And since the volume of Al2O3 that is generating from 1 mole of metal oxidation is sufficient to cover the entire surface, so that means we have a barrier. So that means here initially it was metal aluminum and oxygen, now we have a thin barrier of metal oxide aluminum. So this condition is a very much favorable condition for giving oxidation resistance. Because oxygen does not have a direct contact with aluminum rather oxygen has to somehow reach out to the aluminum surface through the metal oxide.

And that reaching out of oxygen is a complex process it involves diffusion, so we will talk about that diffusion little later. But at least oxygen access to the metal will be difficult and that is what it will have resistance to oxidation. So this is 1 example we can do several such examples in case of chromium. And chromium in case of chromium if we take the chromium data you will see that PBR ratio will come out to be around 2 which is also good even for FeO it will come out to be 1.76, it is also good.

But what I mean to say, now here this 1 mole is important because in this case it becomes half let's say for a FeO the reaction would be

$$2Fe + O_2 = 2FeO$$

So this is the reaction. That case 1 mole generates 1 mole of FeO, so that time this factor will be 1. Now similarly in some cases for example

$$Si + O_2 = SiO_2$$

That case still it is 1 mole and this factor would be 1. So all those cases PBR ratio becomes very straightforward and that time only we have to consider molar volume of that oxide and molar volume of the metal.

But in case of aluminum in case of chromium wherever we have in case of chromium Cr2O3 forms, so there we have to consider this factor there will be a factor which will be not equal to 1, so that factor would be very critical to find out PBR.

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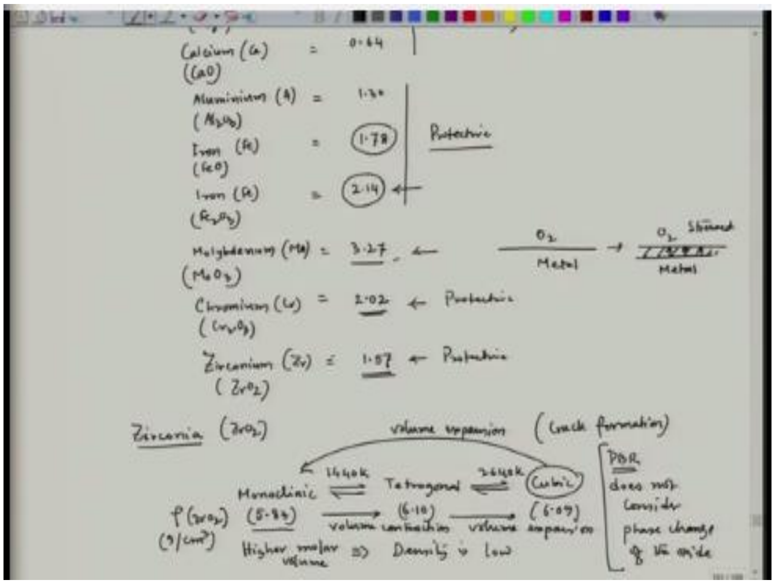

Calcium (Ca) = 0.64
(CaO)
Aluminium (Al) = 1.30
(Al_2O_3)
Iron (Fe) = $\boxed{1.78}$ Protective
(FeO)
Iron (Fe) = $\boxed{2.14}$ ←
(Fe_2O_3)
Molybdenum (Mo) = $\underline{3.27}$ ← $\frac{O_2}{\text{Metal}} \rightarrow \frac{O_2}{\text{Metal}}$ Strained
(MoO_3)
Chromium (Cr) = $\underline{2.02}$ ← Protective
(Cr_2O_3)
Zirconium (Zr) = $\underline{1.57}$ ← Protective
(ZrO_2)

Zirconia (ZrO_2) volume expansion (crack formation)

Monoclinic $\underset{}{\overset{1440K}{\rightleftharpoons}}$ Tetragonal $\overset{2640K}{\rightleftharpoons}$ Cubic

ρ (ZrO_2) (g/cm³) (5.84) → volume contraction (6.10) → volume expansion (6.07)

Higher molar volume ⇒ Density is low

PBR does not consider phase change of the oxide

Now you can calculate for other cases some of the metals where PBR ratio is less than 1 let me note it down. For example, if you take magnesium, so that time if I try to put down all those values magnesium is 0.81 and that time oxide is MgO. Then calcium, so that time oxide is calcium oxide, it will be 0.64. Of course we have seen aluminum and oxide is Al2O3 PBR ratio is 1.3.

Then we can also find out PBR ratio of iron Fe, oxide is FeO, PBR ratio is 1.78, now if you take Fe2O3 PBR would be different. In case of Fe2O3 the PBR ratio would be when this is iron but oxide is Fe it is Fe2O3, that time PBR would be 2.14. So these are the oxides which are protective and if you see 1 in factor in case of FeO it is 1.78 but Fe2O3 it is 2.14 though it is little more than 2.14 but Fe2O3 is very much protective for further oxidation of iron.

Then we have some oxides with much higher value, for example molybdenum where oxide is MoO3 is PBR is 3.27. But in this case of course I will not expect that much of oxidation resistance as per the PBR fundamentals. Then chromium where oxide is Cr2O3 that time PBR becomes 2.02. Now interestingly so that way you can calculate PBR once you know the oxide form then you need to know molecular weight of that oxide, density of that oxide as well as metal atomic weight and metal density.

And from the reaction the balanced reaction we have to find out 1 mole of metal is getting oxidization forming how many moles of metal oxide and that way you can find out. Now interestingly this gives an idea, for example here I can definitely say that it is not covering the entire surface. So it will be exposed to the oxygen all the time we would expect that it will oxidize continuously and at a very high rate.

But in this case I can consider that this is protective, this case I can say that it is not protective. Because once we have a very high volume. Now if let's say the metal oxygen and metal, so that is getting oxidized, this is the oxide layer. And now these oxide layer has got a very high molar volume and since oxides are brittle. So further growth of that oxide would lead to a stress on the particular metal surface, this stressed, because of the further metal oxide formation.

And this stress can lead to cracking on the oxide surface, if the molar volume becomes very high. And then once it cracks definitely it will not be able to protect it. Chromium also it is a protective oxide and that is what we use chromium in stainless steel. And it is PBR ratio is little more than 2 but still we can consider it to be protective. Now interestingly if you see that we have seen that the value if it is 1 to 1.5 to 2 then we can say that it is protective.

But in this case it is little more than 2 but still we say that it is protective because it is close to 2. So that means it will not provide much of stress on the metal oxide layer when further oxidation takes place or the during the oxide growth stage. But here also the same story but here as per the PBR we could say that this is not protected. Now interesting story comes when we talk about PBR ratio of zirconium oxide or zirconia.

So where PBR ratio is in case of zirconium is 1.57 sorry, so this oxide is ZrO2 PBR ratio is 1.57. Now here we say that it is protective very much protective, and of course it is protective but zirconium has a peculiarity. If zirconia is heated there will be phase transformation and these phase transformation leads to problem. So for example if I consider the zirconia phase transformation this is called zirconia ZrO2.

The room temperature phase is monoclinic which has an allotropic transformation to tetragonal. And then again at 2640 K it goes to cubic phase when it goes to and if I try to see the density of the metal oxide, it is here it is 5.83, this is density of ZrO2. Here it is 6.10 and here it is 6.09 and density the unit if I consider gram per centimeter cube. Now interestingly if you see that if the density is low that means it has a higher molar volume if density is low.

If density is low then it will have a higher molar volume and vice versa that means if the density is more molar volume would be less of that oxide. Now you could see that when it goes from monoclinic to tetragonal, we have volume contraction. Again from here to there I have volume expansion, but interestingly zirconia uses at a high temperature. Now if at high temperature we are using that zirconia in the form of tiles or something at a high temperature heat-resistant material.

So there it will have a cubic structure and once it is cooled from this to monoclinic, I will have volume expansion. And this volume expansion would lead to crack formation and once the crack forms then the oxide will try to break off. Now even if zirconia is protective still I could see that as per the PBR ratio, I could see that this volume expansion due to or volume expansion or volume contraction due to change in structure we are not considering.

So that means PBR does not consider phase change of the oxide, fine. So since it is not considering phase change, it is not going to tell us the actual picture the way it is happening in case of zirconia. That high temperature phase will not be stable at room temperature low temperature and that time cubic to monoclinic transformation would lead to volume expansion and that would create crack in the zirconia.

Now of course if you add yttrium or magnesium or calcium to the zirconia it tries to stabilize cubic phase at room temperature. So that is what we avoid that phase transformation and that would lead to a stability in the zirconia that crack formation would not happen because the volume expansion in the oxide layer. And that is what we use zirconia yttria stabilized zirconia which stabilizes high temperature phase down to room temperature. But from the PBR aspect it does not consider this phenomena, like that PBR does not consider many other things.

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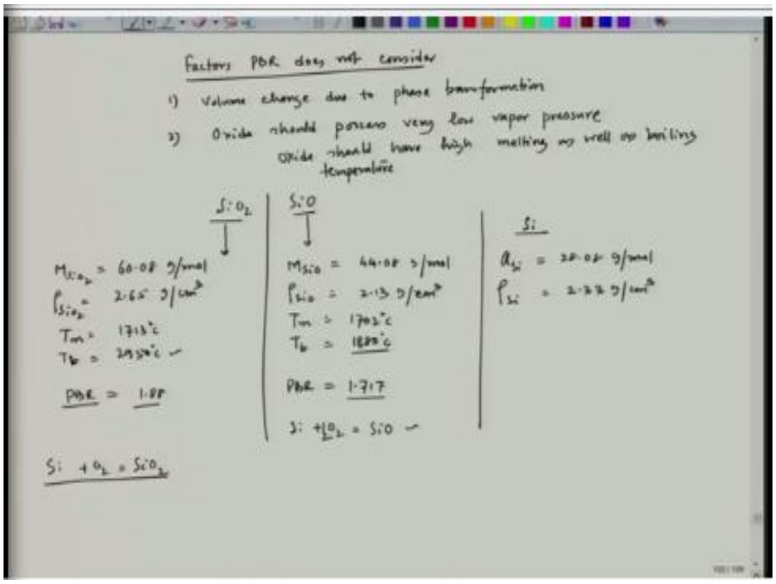

Factors PBR does not consider

1) Volume change due to phase transformation

2) Oxide should possess very low vapor pressure
Oxide should have high melting as well as boiling temperature

SiO_2

$M_{SiO_2} = 60.08$ g/mol
$\rho_{SiO_2} = 2.65$ g/cm^3
$T_m = 1713$°C
$T_b = 2950$°C
PBR = 1.88

$Si + O_2 = SiO_2$

SiO

$M_{SiO} = 44.08$ g/mol
$\rho_{SiO} = 2.13$ g/cm^3
$T_m = 1702$°C
$T_b = 1880$°C
PBR = 1.717

$Si + \frac{1}{2}O_2 = SiO$

Si

$A_{Si} = 28.08$ g/mol
$\rho_{Si} = 2.33$ g/cm^3

Like let’s note down all those factors what PBR does not consider, volume change due to phase transformation. Since it only bothers about the volume of the oxide and the volume of the metal, it does not consider the phase change or allotropic transformation in the metal in that oxide. Second part, now in order to for example in case of 1 metal PBR ratio is around 1.5, but if that oxide has a low vaporization temperature then that would lead to a problem.

So that problem can be for example even if it is having very favorable PBR but high temperature it will vaporize because it has a very high vapor pressure. Since its boiling point is low, that is also not considered in case of PBR. So oxide should possess very low vapor pressure or I could say that it should have oxide should have high melting as well as boiling temperature, this is not considered in case of PBR, the classic example is silicon oxide and these 2 oxides.

So when we talk about silicon oxide, then let’s calculate the PBR for both the cases. In case of silicon oxide, the data if I consider SiO2 = 60.08 gram per mole Rho = 2.65, Tm =1713 degree Celsius T boiling 2950 degree Celsius. And here MSiO this is 44.08 gram per mole 2.13 Tm = 1702 degree Celsius but Tb which is the boiling temperature is 1880 degree Celsius. Now if I try to calculate PBR from a Silicon data, this is atomic weight of silicon is 28.08 gram per mole.

Then we have a Rho is 2.33 meter cube, so here PBR for the reaction

$$Si + O_2 = SiO_2$$

would be 1.88 and here PBR would be equal to the reaction would be it will be 1.717. So now I could see that the PBR in both the cases it is closed a line, but interestingly because this has boiling.1880 degree Celsius and here the silicon oxide is 92950 degree Celsius. So this one would try to evaporate and once it evaporates there will be no oxide layer sticking to the surface and it will expose the metal surface for further oxidation, so these particular factors are not considered in PBR.

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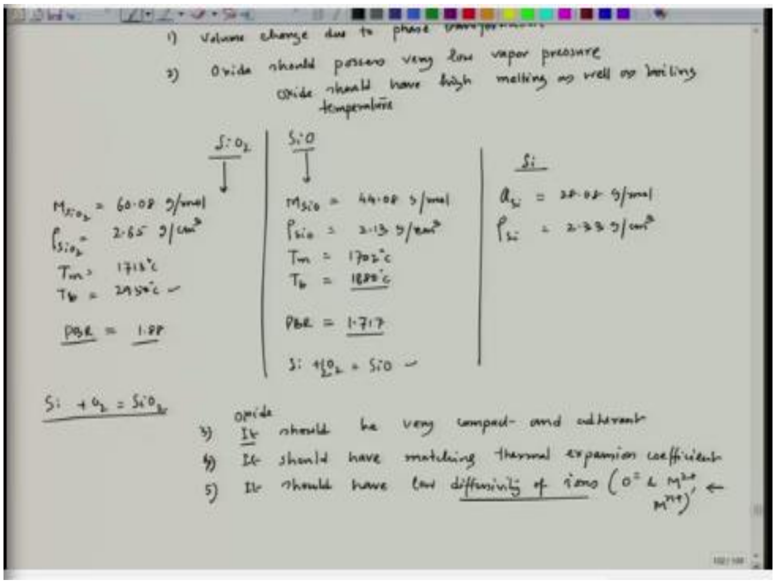

1) Volume change due to phase

2) Oxide should possess very low vapor pressure
oxide should have high melting as well as boiling temperature

SiO_2

M_{SiO_2} = 60.08 g/mol
ρ_{SiO_2} = 2.65 g/cm^3
T_m = 1713°C
T_b = 2950°C
PBR = 1.88

$Si + O_2 = SiO_2$

SiO

M_{SiO} = 44.08 g/mol
ρ_{SiO} = 2.13 g/cm^3
T_m = 1702°C
T_b = 1880°C
PBR = 1.717
$Si + \frac{1}{2}O_2 = SiO$

Si

a_{Si} = 28.08 g/mol
ρ_{Si} = 2.33 g/cm^3

3) It (oxide) should be very compact and adherent
4) It should have matching thermal expansion coefficient
5) It should have low diffusivity of ions (O^{2-} & M^{2+}, M^{n+})

So there are other factors like for a oxide to be protective it should be very compact and adherent, fourth it should have matching expansion coefficient or I would say thermal expansion coefficient, then it means oxide, so it should have low diffusivity of ions and here I am considering O2- and metal 2 + or I can even consider metal n + for example in case of aluminum it will be Al3 + in case of chromium it is Cr3 + whereas in case of iron it could be either Fe2 + or Fe3 +.

So these ions would have a very low diffusivity, that means the defect concentration in the metal oxide should be less, ok. So these factors are not considered in the PBR ratio, so that is what the PBR ratio can give you an indication that some oxide could be protective or not but that will not be definite. So in order to have a definite approach one has to study the oxide layer it is other characteristics like diffuse the defect concentration in the oxide.

Like what is the melting point boiling point, what could be the thermal expansion coefficient and whether it is adherent or not whether it is compact or not. So those factors we have to study we have to understand one by one. But for our understanding we will look at this particular issue a little greater and rest of the thing will not touch for the time being.

But these factor the diffusivity of ions factor will consider that will explain us which surface would grow whether metal oxide interface would have oxide formation or oxide oxygen interface would have oxide formation. That can be told if we know the defect information in the oxide as well as the diffusivity information in the oxide. So let me stop here we will continue our discussion on the oxidation of metals and alloys in subsequent lectures, thank you very much.