Steel Making

Prof. Deepak Mazumdar
Prof. S. C. Koria
Department of Material Science and Engineering

Indian Institute of Technology, Kanpur

Module No. # 01

Lecture No. # 11

Modern Steelmaking I, Oxygen Steelmaking

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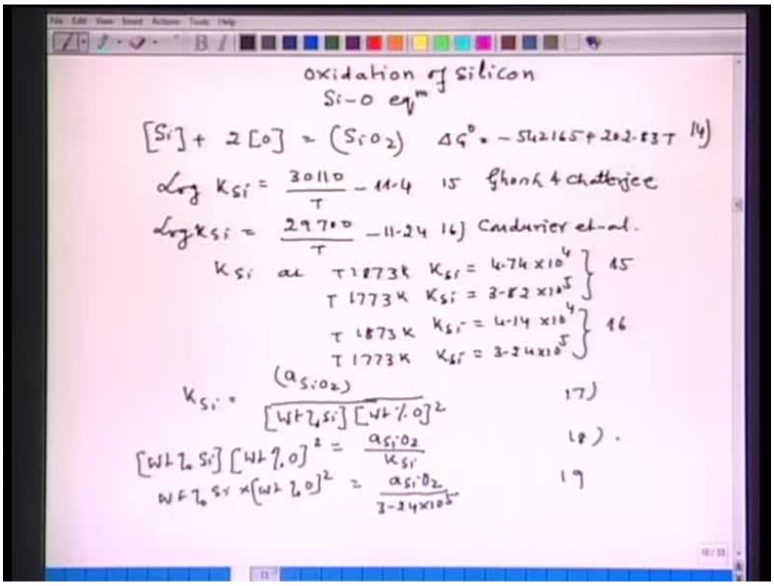

oxidation of silicon
Si–O eq^m

$[Si] + 2[O] = (SiO_2)$ $\Delta G^0 = -542165 + 202.83T$ 14)

$\log K_{Si} = \frac{30110}{T} - 11.4$ 15 Ghosh & Chatterjee

$\log K_{Si} = \frac{29700}{T} - 11.24$ 16) Cadurier et al.

K_{Si} at T 1873K $K_{Si} = 4.74 \times 10^4$ } 15
T 1773K $K_{Si} = 3.82 \times 10^5$ }
T 1873K $K_{Si} = 4.14 \times 10^4$ } 16
T 1773K $K_{Si} = 3.24 \times 10^5$ }

$K_{Si} = \frac{(a_{SiO_2})}{[wt\%Si][wt\%O]^2}$ 17)

$[wt\%Si][wt\%O]^2 = \frac{a_{SiO_2}}{K_{Si}}$ 18).

$wt\%Si \times [wt\%O]^2 = \frac{a_{SiO_2}}{3.24 \times 10^5}$ 19

So, next reaction is oxidation of silicon. In fact, we are considering silicon oxygen equilibrium. So, if I write the reaction, silicon plus 2 O, that is equal to Si O 2. This rounded brackets, I am using for slag, and square bracket, I am using for dissolved in metal. Delta G naught, the value is minus 542165 plus 202.83T. Now, this is equation number 14.

Now, remember this reaction is highly exothermic in nature. Now, about log of K silicon, that is equal to 30110 upon T minus 11.4. Now, there are different sources. I have given slightly different values. I thought to give you the value of log K silicon from other sources also. So, log of K silicon from other sources is 29700 upon T minus 11.24. In fact, this is equation 15. This is equation 16.

15, I have taken from the book of Ghosh and Chatterjee, the reference I have given at the end of this lecture. And this, I have taken from the book Coudurier et al, again the reference I have given at the end of the chapter

So, now, if I just calculate the value of, let us say, now, I calculate K silicon for example, at temperature 1873, then K silicon, that comes around 4.74 into 10 to the power 4 and if I calculate T, 1773, then I get K silicon that is equal to 3.82 into 10 to the power 5 and this is from equation 15. Now, the same value of K silicon, I calculate from equation 16, then I get T 1873 Kelvin, they are all Kelvin, then K silicon is here 4.14 into 10 to the power 4 and at temperature 1773 Kelvin, K silicon, that is equal to 3.24 into 10 to the power 5. So, this is from 16.

So, what I wanted to tell you, that you may be come across with the different sources and you may get slightly different value. So, accordingly I gave you, just for the reference, but, both the equation predict that, the decreasing temperature increases the value of K silicon. That is our conclusion that we get at different temperatures.

Now, if I write down the value of K from equation 14, then I get K silicon, that is equal to activity of Si O 2 in slag, recall, weight percent silicon in metal into weight percent O square. And let us put it, this equation as 17.

Now, if I write, the weight percent silicon, weight percent oxygen squared, that is equal to, activity of Si O 2 upon K silicon. Let us put this equation as 18. So, we can see that oxidation of silicon is favored at low temperature. So, if I put the value of K, for example, K silicon at 1773, then weight percent silicon into weight percent squared that is equal to activity of Si O 2 upon 3.24 into 10 to the power 5, and let us take it, this equation as 19..

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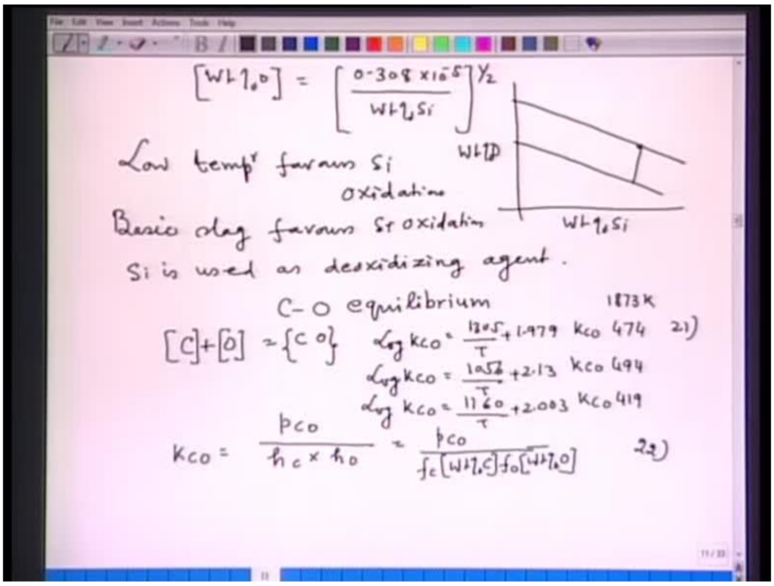

$$[Wt\%O] = \left[\frac{0.308\times10^{-5}}{Wt\%Si}\right]^{1/2}$$

Low temp^r favours Si oxidation

Basic slag favours Si oxidation

Si is used as deoxidizing agent.

C – O equilibrium 1873K

$[C]+[O] = \{CO\}$ $\log K_{CO} = \frac{1305}{T} + 1.479$ K_{CO} 474 21)

$\log K_{CO} = \frac{1056}{T} + 2.13$ K_{CO} 494

$\log K_{CO} = \frac{1160}{T} + 2.003$ K_{CO} 419

$$K_{CO} = \frac{p_{CO}}{h_c \times h_o} = \frac{p_{CO}}{f_c[Wt\%C]\,f_o[Wt\%O]} \quad 22)$$

So, we write down now, weight percent oxygen, that is equal to 0.308 into 10 to the power minus 5 upon weight percent silicon raised to the power 1 by half.

So, if I plot now, the weight percent oxygen against weight percent silicon, now, this will be for 1773 Kelvin or 1500 degree Celsius, then I will get a straight line with the slope equal to minus half.

So, all that it says, that increase in silicon decreases the oxygen, as this equation predicts. Now, if I take another temperature for example, 1800 degree centigrade, then probably, then I may get, this particular equation. That is, increase in temperature, it does not allow silicon reaction to proceed. That means a decrease in temperature favors the reaction of silicon.

Also, if we see this equation number 17, we see that if we decrease the activity of Si O 2, then silicon reaction is favored. So, what we can conclude from here, that in a steel refining, silicon oxidation is very fast and silicon oxidized before any other impurities, because, the heat of formation of Si O 2 is very very large, that means highly exothermic reaction.

Second thing is that, low temperature favored silicon oxidation and basic slag also favors silicon oxidation. Why, because if the slag is basic, the activity of Si O 2 is drastically reduced, and hence the basic slag favors the reduction of silicon in the metal..

Now, therefore, because of its very strong affinity, of silicon with oxygen, now silicon is used as a deoxidizing agent also. Now, for example, if a steelmaking with acid slag, the activity of Si O 2 is very high and hence silicon reduction or the silicon oxidation, it does not proceed that fast, as compared to, when you have the basic slag.

Now, next let us consider, the carbon oxygen equilibrium. Next, consider carbon oxygen equilibrium, also called oxidation of carbon. Now, this oxidation of carbon is the most important reaction in a steel making.

Now, let us consider the reaction. For example, C plus O that is equal to CO and here again, I could get the different values of K CO from the literatures I am giving you, leaves a log of K CO, that is equal to 1305 upon T plus 1.979. If I calculate at 1873 Kelvin, the value of K CO, that becomes equal to 474. Let us call this equation as 21.

Now, if I take another source, which gives log of K CO, that is equal to 1056 upon T plus 2.13. Now, here I get K CO 494.

If I take even another source, log of K CO, that is equal to 1160 upon T plus 2.003. Here I get K CO is equal to 419. Now, what I wanted to say, that depending on the source, these value of K CO it may differ and the reference of all the source, I have given in the, at the end of the lecture, under the term, references for further reading.

Now, to understand the carbon oxygen equilibrium, let us write down the value of K. So, K CO that will be equal to, p CO upon h c into h o, now, recall the solute elements in liquid steel, they obey Henry law.

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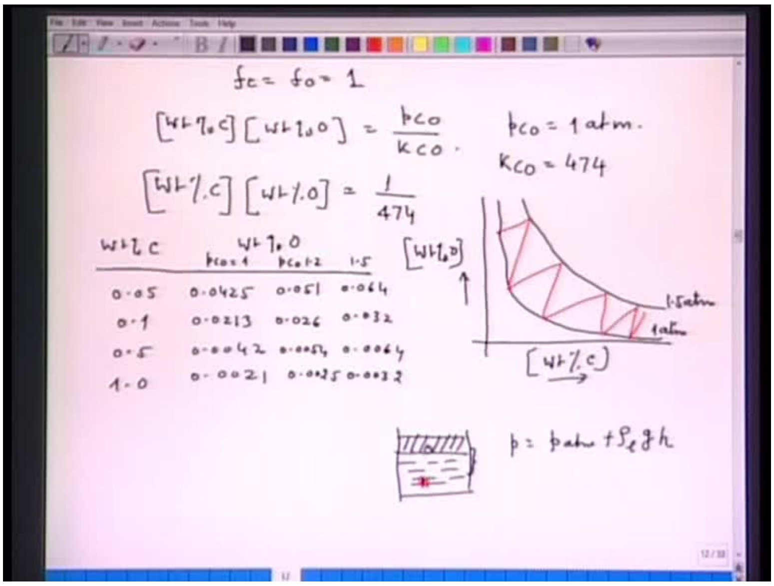

$f_C = f_O = 1$

$[wt\%C][wt\%O] = \frac{p_{CO}}{K_{CO}}$.

$p_{CO} = 1$ atm.

$K_{CO} = 474$

$[wt\%C][wt\%O] = \frac{1}{474}$

wt% C	wt% O $p_{CO}=1$	 $p_{CO}=2$	 1.5
0.05	0.0425	0.051	0.064
0.1	0.0213	0.026	0.032
0.5	0.0042	0.0051	0.0064
1.0	0.0021	0.0025	0.0032

$p = p_{atm} + \rho_e g h$

So, accordingly I will write down p CO, f C into weight percent carbon, f O weight percent oxygen and let us call this equation as 22. Now, assuming, the activity coefficient of carbon and oxygen in liquid steel to be unity, however, this value may not be unity, but, for the sake of calculation and understanding, let us take that f C is equal to f O, that is equal to 1.

And, if I substitute this value into the equation number 22, then I get weight percent carbon into weight percent oxygen, that is equal to p CO upon K CO. Now, this equation suggests that, the product of weight percent carbon and weight percent oxygen, it depends upon partial pressure of carbon mono oxide and the value of KCO.

Now, if we take for example, p CO, let us take it 1 atmosphere and let us take the value of K CO, that is equal to, for example, 474. Now, if we do that, then what we get from here, that weight percent C into weight percent O, that is equal to 1 upon 474. Now, this value of 474 is at 1873 Kelvin. What we can do, so, if we plot for example, say weight percent O upon weight percent carbon, then what we get, is this sort of relationship. This is just a schematic relationship. So, weight percent carbon increases from here and weight percent oxygen, it increases in this direction. So, what this reaction says or what this plot suggests, that as the weight percent carbon increases, the weight percent oxygen dissolved in steel it decreases. Also, this plot suggests, that at low percent carbon in steel the dissolution of oxygen increase also. Because, if you see, at the lower ranges of carbon, the dissolution of the oxygen, it increases very fast.

Now, for example, if I calculate, take weight percent carbon and take here, weight percent oxygen and I calculate for different p CO values. So, I take p CO 1 atmosphere, 1.2 atmosphere and 1.5 atmosphere. So, if I do that, I put here the p CO is equal to 1 atmosphere, p CO 1.2 and p CO 1.5, I take 0.05 percent carbon 0.1, 0.5 and 1.0.

So, I calculate here, 0.0425, 0.0213, 0.0042 and 0.0021. At p CO is equal to 1.2 atmosphere, 0.051, 0.026, 0.0054 and 0.0025, p CO is equal to 1.2 atmosphere. P CO is equal to 1.5 atmosphere, I calculate 0.064, 0.032, 0.0064 and 0.0032.

So, what this calculation suggests, that increase in the partial pressure of carbon mono oxide, it increases the dissolved oxygen content in steel. So, if I plot these values or if I just show schematically these values, that this is at 1 atmosphere p CO, then somewhere here, I should have 1.5 atmosphere, and this particular range may have the range of partial pressure of CO.

So, what I want to say from here is that, that increase in partial pressure of carbon mono oxide, it increases the oxygen dissolved in steel. Now, you must be wondering, what does it mean?

Now, for example, if I consider a bath, is a hot metal bath. This is hot metal and from here, for example, a nucleation site is somewhere here, and here carbon mono oxide bubble is evolved. So, at this particular location, if this is the nucleating site for nucleation of C and O, that is equal to CO bubble, then the partial pressure or the total pressure on this bubble will be equal to p, that will be equal to p atmosphere plus this column pressure, that is rho l g h, where h is the bath height.

So, what this says? If the nucleation of C plus O is equal to CO bubble, occurs deep in the bath, then on account of the ferro-static pressure plus atmospheric pressure that this bubble is exerted, because of that, the dissolution of oxygen in the bath is increases.

Now, in another situation, for example, if the nucleating site, for example, here, say here somewhere, here if we have the slag, so if the nucleating site is at the slag metal interface, then we can consider the nucleating bubble will be experiencing only atmospheric pressure, for example, equal to 1 atmosphere. So, between the range, where the CO bubble is nucleating, depending on that, the dissolved oxygen in steel, it may vary.

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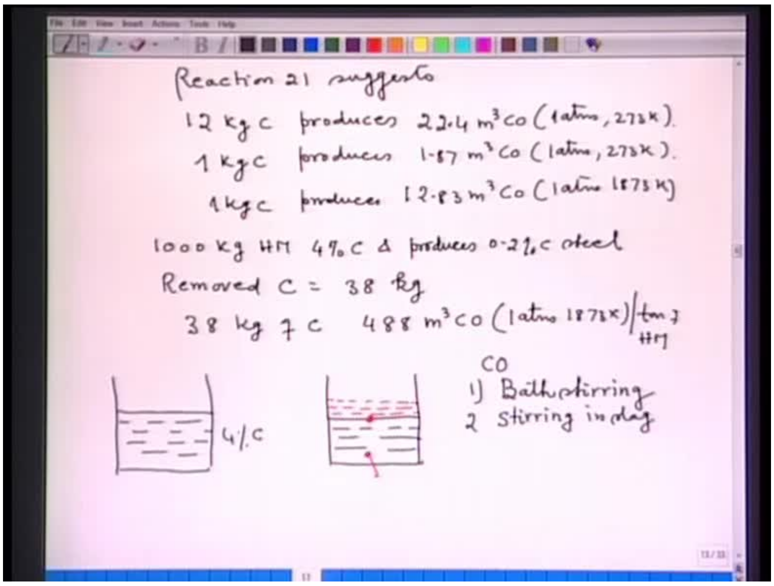

Reaction 21 suggests

12 kg C produces 22.4 m^3 CO (1 atm, 273K).

1 kg C produces 1.87 m^3 CO (1 atm, 273K).

1 kg C produces 12.83 m^3 CO (1 atm 1873 K)

1000 kg HM 4% C & produces 0.2% C steel

Removed C = 38 kg

38 kg of C 488 m^3 CO (1 atm 1873K)/ton of HM

CO

1) Bath stirring

2 stirring in slag

So, now this reaction 21 suggest, what it suggests, say 12 kg carbon produces 22.4 meter cubed carbon mono oxide at 1 atmospheric pressure and 273 Kelvin.

Therefore, 1 kg carbon produces 1.87 meter cubed carbon mono oxide at 1 atmospheric pressure and 273 Kelvin. This particular volume of CO at 1873, it will become 12.83 meter cubed CO at 1 atmosphere and 1873 Kelvin, that is 1 kg carbon produces 12.83 meter cubed CO at 1 atmospheric pressure and 1873 Kelvin.

Now, suppose if I have 1000 kg hot metal, which contains a 4 percent carbon and I am produces 0.2 percent carbon steel, then what I am doing, then I am removing 38 kg of carbon.

Now, this 38 kg of carbon, so removed carbon, that is equal to 38 kg. Now, this 38 kg of carbon will produce 488 meter cubed of carbon mono oxide, when calculated at 1 atmosphere and 1873 Kelvin and mind here friend, this is per ton of hot metal. Of course, this amount of CO will be evolving over a period of time. It is not that, suddenly it will evolve, it will evolve over a period of time. So, you can think of, that this reaction is very very important in case of a steel making.

So, you can also imagine that, this reaction is, suppose we consider 100 ton of hot metal, then for 100 ton of hot metal, you can calculate the amount of CO that will be evolving and hence the uninterrupted exit of CO gas must be ensured during refining of hot metal to steel. Now, with this what I mean is, as follows.

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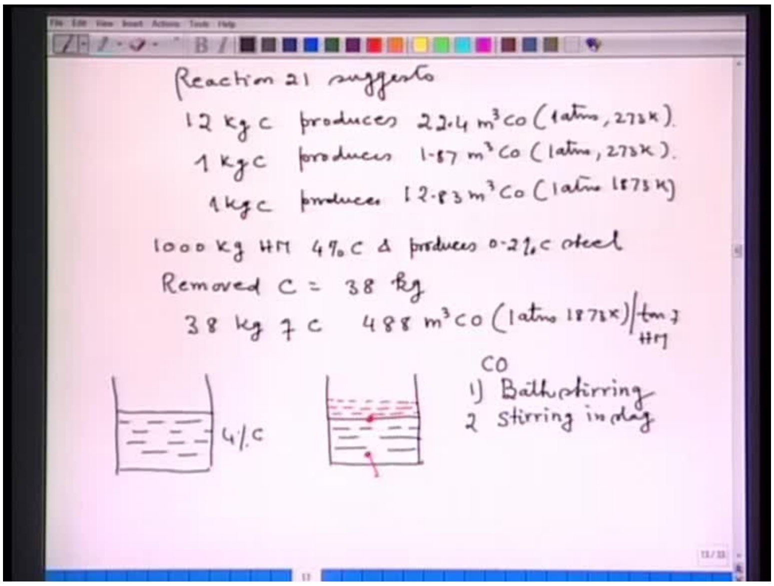

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Removed C = 38 kg

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CO

1) Bath stirring

2 stirring in slag

Now, for example, again I take a steel bath. It is hot metal, containing four percent carbon. I am providing oxygen. There is no clay cover in the beginning, then whatever the amount of CO which is evolving due to oxidation of carbon will be exiting uninterruptedly and continuously from the bath, because there is no hindrance. So, that is one extreme.

Now, another extreme, consider the situation, I have here metal bath and on the top I have slag. Slag will form, because this supply oxygen iron will oxidize to Fe O.

So, now the amount of CO that we will calculate over the period of time, it should find its path for the exit uninterruptedly and continuously. That means the slag cover which is on the top of the molten steel, it should not hinder the free passage of carbon mono oxide. If it does, then slag will form, and if no care is been taken, then slag will come out from the vessel and that is a very, that is not at all desired for refining of hot metal to steel.

Now, another situation you can also consider, for example, if the nucleating site is at the slag metal interface, then the bubbles will not have sufficient time to grow, the bubbles will be smaller in size, on account of which the slag will foam..

In another situation if the carbon oxygen reaction is deep seated in the bath, that is somewhere here, then the carbon mono oxide bubble will have sufficient time to grow, their size will be greater and hence they will find an easy step.

What I wanted to communicate here, that this carbon oxygen reaction is very important because, carbon mono oxide is a gaseous product. If its exit is interrupted by someway, it can be interrupted, for example, by the viscosity of the slag, if the slag is highly viscous, then the bubbles are trapped into the slag and the slag will foam and that is not at all desired. So, what is being important, for the gaseous product to exit, if the bath is covered by slag cover, the slag should have the properties which provide an easy escape of CO bubble during the entire refining period, because the large volume of CO bubble will be evolving as you have seen in this particular calculation. Number 1.

Number 2, since the carbon mono oxide, it forms a gas, on its exit from the bath to the atmosphere, it will also provide stirring to the bath. So, what I mean to say, that this CO reaction, or the product CO which is forming, it will provide bath stirring. And, stirring of the bath will eliminate a concentration and temperature gradient. So, these are all the advantages. Another thing, as this CO exits through the slag, it will also provide stirring in the slag.

So, what are the advantages associated with the stirring of the slag? Suppose, you have made a slag and you want to add something for the dissolution in the slag, then because of the good stirring, it will try to eliminate the gradient and hence dissolution rate will be faster.

So, these are the some of the advantages of the C plus O is equal to CO reaction, but, at the same time, if easy escape of CO bubble is not guaranteed during their exit, then the slag will foam and it may come out from the vessel and this particular phenomenon is undesirable and it is called slopping, because it leads to large amount of metal also, along with it. So, that point is to be kept in mind, while we convert this knowledge into the practice.

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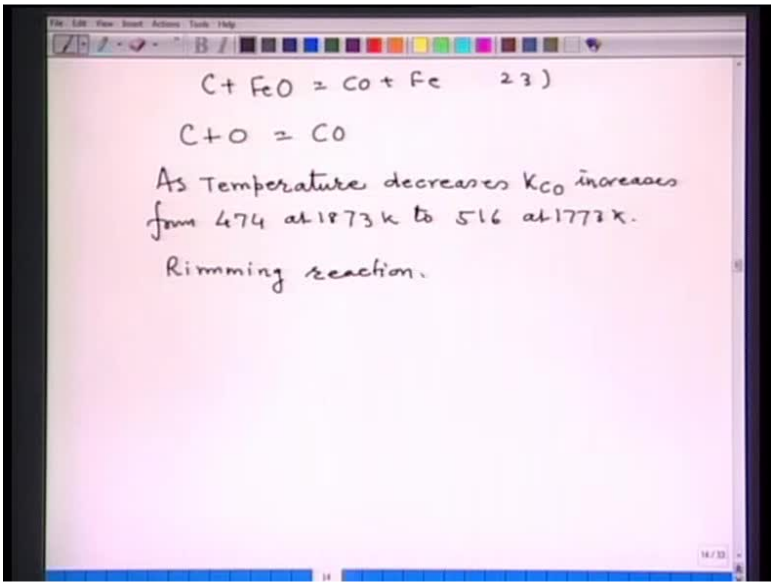

$C + FeO = CO + Fe$ 23)

$C + O = CO$

As Temperature decreases K_{CO} increases from 474 at 1873 K to 516 at 1773 K.

Rimming reaction.

Now, another important reaction that also can occur, is carbon with the Fe O. So, for example, carbon plus Fe O, that is equal to CO plus Fe. Let us take this reaction is 23. Now, this reaction may cause slag to foam, why, because this reaction will be occurring at the slag metal interface or within the slag. The bubbles will not have a sufficient time to grow, their size will be smaller, on account of which the slag may foam, if the properties of slag are not suitable for the easy escape of the carbon mono oxide bubble.

For this purpose, slag properties, its formation, they are also an important part of steel making. Now, this reaction C plus O is equal to CO, has also importance during solidification of steel.

Now, say as temperature decreases, for example, K CO it increases from 474 at 1873 Kelvin to 516 at 1773 Kelvin.

What does it mean? So, increase in K will decrease weight percent carbon into weight percent oxygen, as you can note from the equilibrium reaction.

What does it mean? If the weight percent carbon and weight percent oxygen decreases with the decreasing temperature, then CO evolution will occur during solidification. Because, when the steel solidifies, the temperature decreases. On account of decrease in temperature, because of the equilibrium consideration, the carbon mono oxide reaction will occur during solidification and this phenomenon is called rimming reaction.

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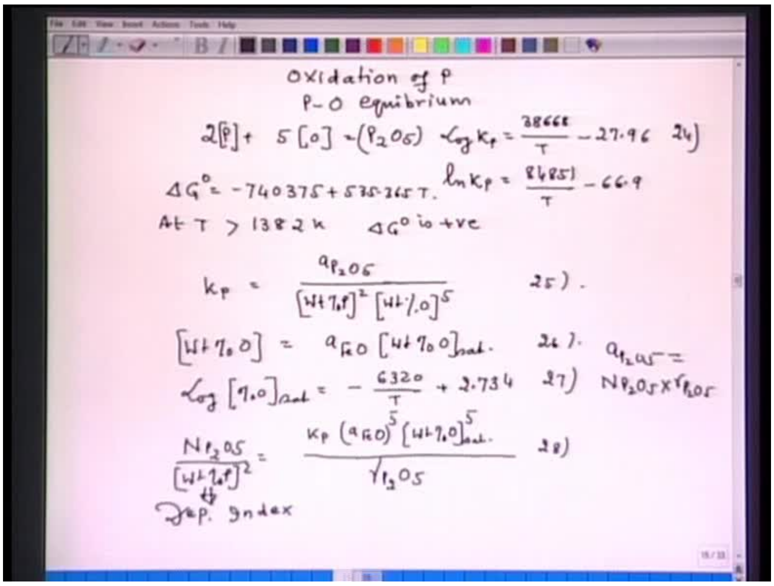

Oxidation of P

P-O equilibrium

$$2[P] + 5[O] = (P_2O_5) \quad \log K_P = \frac{38668}{T} - 27.96 \quad 24)$$

$$\Delta G^\circ = -740375 + 535.365\,T. \quad \ln K_P = \frac{84851}{T} - 66.9$$

At T > 1382 K ΔG° is +ve

$$K_P = \frac{a_{P_2O_5}}{[\text{wt}\,\%\,P]^2\,[\text{wt}\,\%\,O]^5} \quad 25).$$

$$[\text{wt}\,\%\,O] = a_{FeO}\,[\text{wt}\,\%\,O]_{sat}. \quad 26).$$

$$a_{P_2O_5} = N_{P_2O_5} \times \gamma_{P_2O_5}$$

$$\log[\%O]_{sat} = -\frac{6320}{T} + 2.734 \quad 27)$$

$$\frac{N_{P_2O_5}}{[\text{wt}\,\%\,P]^2} = \frac{K_P\,(a_{FeO})^5\,[\text{wt}\,\%\,O]^5_{sat}}{\gamma_{P_2O_5}} \quad 28)$$

$\Downarrow$ Dep. Index

So, let us consider the next reaction, oxidation of phosphorous, or phosphorous oxygen equilibrium. That is 2 P in metal plus 5 O that is equal to P 2 O 5 in slag. Log of K P, that is equal to T minus 27.96. This is called equation number 24. Now, again I could get another source also, which says this l n K P, that is equal to 84851 upon T minus 66.9.

Now, remember this equation is l n. Earlier equation is in terms of log. So, if we calculate from both these values at a particular temperature, the value of K will come slightly different, but, the trend of prediction with the temperature is same in both cases. Only I want to give you, depending on the source which you take for your calculation, the values may differ slightly.

Now, for this reaction, delta G naught, that is equal to minus 740375 plus 535.365 T. Now, at temperature T is greater than 1382 Kelvin, delta G naught is positive.

What does it mean? P 2 O 5 will decompose and phosphorous will revert into the bath. Therefore, P 2 O 5 or the activity of P 2 O 5 must be decreased drastically. If we do not decrease the activity of P 2 O 5, then whatever P 2 will 5, and then whatever P 2 O 5 will form it will immediately decompose and the phosphorous reversal will be there.

So, if I write down the value of K P, K P will be equal to activity of P 2 O 5 upon weight percent P squared, weight percent O to the power 5. Let me put this reaction as 25.

Now, we also know that weight percent O, that is equal to activity of Fe O into weight percent O saturated. Take it 26 and in earlier lecture, we have seen log of percent O saturated, that is equal to minus 6320 upon T plus 2.734, that is, let us take equation number 27.

So, by equation 25 and 26, we can replace weight percent oxygen in equation 25 by using equation number 26. Then we get, and after rearrangement, then we get N P 2 O 5 upon weight percent P squared, that is equal to K P activity of Fe O to the power 5, weight percent O to the power 5 saturated upon gamma P 2 O 5. Let us call this equation 28. What I have done in this equation, I have replaced activity of P 2 O 5, that is equal to N P 2 O 5 into gamma P 2 O 5.

Now on the assumption that, this slag obeys the Routes' law and hence gamma P 2 O 5 is the activity co efficient of P 2 O 5. Now, this ratio N P 2 O 5 upon weight percent P to the power square, it denotes the dephosphorization index, that is this ratio, can call, I am just writing d e p, means dephosphorization. This is dephosphorization index, because N P 2 O 5 is approximately proportional to weight percent phosphorous in slag.

You can call this ratio dephosphorization index or coefficient of phosphorous partition or dephosphorization ratio, whichever way is convenient to you. What we want? Higher values of N P 2 O 5 upon weight percent P needs, low value of gamma P 2 O 5. Because, we want to remove phosphorous from the hot metal.

If we want to remove phosphorous from the hot metal, then the ratio N P 2 O 5 upon weight percent P must very large and in order that, this ratio should be large, gamma P 2 O 5 should be very low, for a given activity of Fe O and given dissolved oxygen content in the bath.

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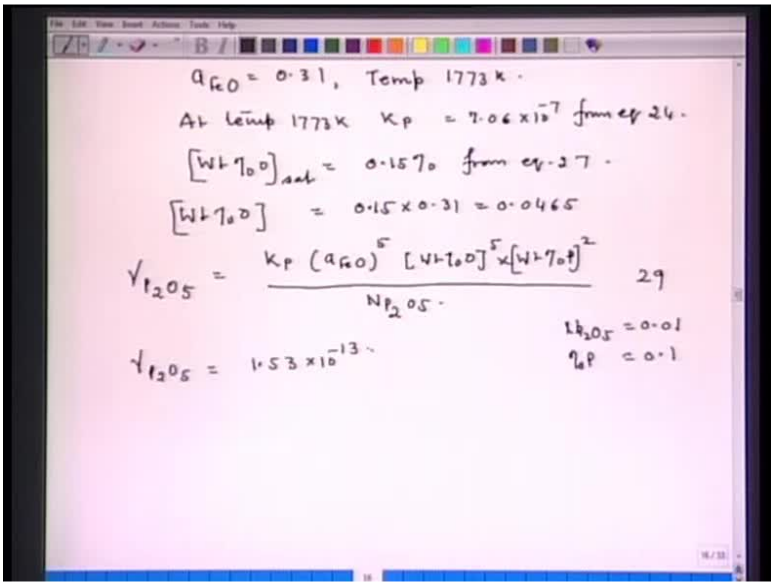

$a_{FeO} = 0.31$, Temp 1773 K.

At temp 1773 K $K_P = 7.06 \times 10^{-7}$ from eq 24.

$[\text{Wt}\%\text{O}]_{sat} = 0.15\%$ from eq. 27.

$[\text{Wt}\%\text{O}] = 0.15 \times 0.31 = 0.0465$

$$\gamma_{P_2O_5} = \frac{K_P\,(a_{FeO})^5\,[\text{Wt}\%\text{O}]^5 \times [\text{Wt}\%\text{P}]^2}{N_{P_2O_5}} \qquad 29$$

$N_{P_2O_5} = 0.01$

$\%P = 0.1$

$\gamma_{P_2O_5} = 1.53 \times 10^{-13}$

Now, let us consider, say a situation, for example, consider activity of Fe O that is equal to 0.31. That means you have created a slag, which has activity of Fe O equal to 0.31.

Let us consider, temperature equal to 1773 Kelvin. Then we can calculate a temperature, 1773 Kelvin K P that is equal to 7.06 into 10 to the power minus 7. This is from equation 24. However, if you calculate from other equation, this, this value will be something different.

Now, I can calculate also, weight percent oxygen saturated. That will be equal to 0.15 percent and that I have calculated from equation 27. Then weight percent oxygen, that will be equal to 0.15 into 0.31, that will be 0.0465. You can also calculate, because we did this calculation earlier.

Now, I substitute all these values and try to know, what value of gamma P 2 O 5 I would require, to remove phosphorous from metal to slag or other way round, to increase the ratio of N P 2 O 5 upon weight percent P square. That is what I am trying to calculate.

Now, if I substitute all these values into equation, say 28, then I will be getting gamma P 2 O 5, that will be equal to K P activity of Fe O to the power 5, weight percent O to the power 5 into weight percent P to the power square upon N P 2 O 5. Now, this equation, I have just rearranged the equation 28.

Now, suppose I consider say N P 2 O 5, say this is 0.01, percent phosphorous I consider let us 0.1. Now, if I substitute all these values into this, then I will get gamma P 2 O 5, that comes out to be equal to 1.53 into 10 to the power minus 13.

Such a low value of gamma P 2 O 5 can be attained by a basic slag, since basic slag has a strong affinity with P 2 O 5, so the activity coefficient of P 2 O 5 can be drastically reduced. Now, the differential basic oxides have different ability to lower gamma P 2 O 5 as shown in the following equation.

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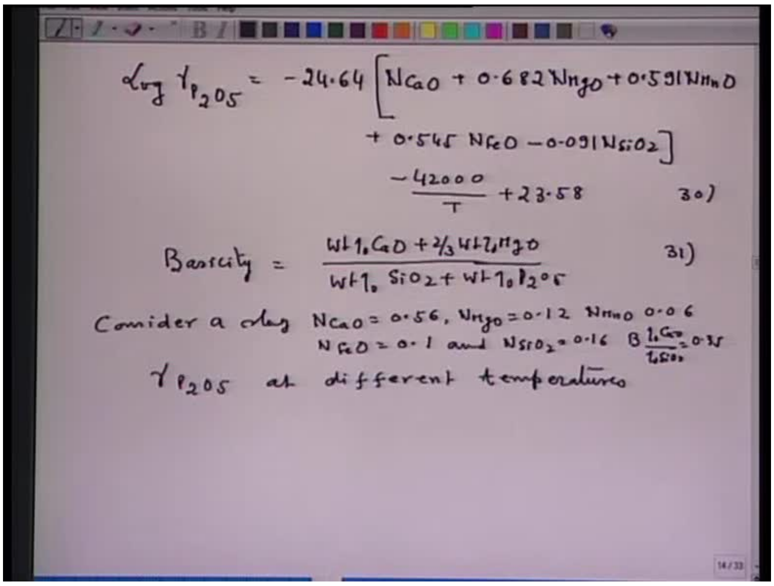

$$\log \gamma_{P_2O_5} = -24.64\left[N_{CaO} + 0.682 N_{MgO} + 0.591 N_{MnO} + 0.545 N_{FeO} - 0.091 N_{SiO_2}\right] - \frac{42000}{T} + 23.58 \qquad 30)$$

$$\text{Basicity} = \frac{\text{wt\% CaO} + 2/3\ \text{wt\% MgO}}{\text{wt\% SiO}_2 + \text{wt\% P}_2\text{O}_5} \qquad 31)$$

Consider a slag $N_{CaO} = 0.56$, $N_{MgO} = 0.12$ N_{MnO} 0.06 $N_{FeO} = 0.1$ and $N_{SiO_2} = 0.16$ $B\ \frac{\%CaO}{\%SiO_2} = 0.35$

$\gamma_{P_2O_5}$ at different temperatures

Log gamma P 2 O 5, that is equal to minus 24.64 N Ca O plus 0.682 N MgO plus 0.591 N MnO plus 0.545 N Fe O minus 0.091 N SiO 2 minus 42000 T, now here the T is in Kelvin, plus 23.58 and this is equation number 30.

Now, in the equation 30 you see that, Mg O is around 0.682 times as effective as that of calcium oxide. That means if the calcium oxide effectivity is 1 then, Mg O is only 0.68 times as effective as that of calcium oxide.

So, in relation to this, the basicity can be defined as equal to weight percent Ca O plus 2 by 3 weight percent Mg O upon weight percent Si O 2 plus weight percent P 2 O 5 and this is equation number 31.

This basicity in this particular form, it expresses the effectivity of different basic oxide on, for example, dephosphorization. As you see from this equation 30, that Mg O is only

0.8, 0.68 times effective as that of calcium oxide. Mn O is 0.59 times effective, Fe O is of the similar order of magnitude, whereas, Si O 2 has a negative influence on dephosphorization. This is the important thing..

Na 2 O and Ba O, they are even stronger than calcium oxide, but, they corrode the lining and hence they are not very often used in the practice. Consider a slag N Ca O. Let us take it equal to 0.56, N Mg O 0.12, N Mn O 0.06, N Fe O that is equal to 0.1 and N Si O 2 that is equal to 0.16, and the basicity as defined by percent Ca O upon percent Si O 2, that is equal to 0.35 or we can say N Ca O upon N Si O 2 is equal to 3.5. Now, let us calculate gamma P 2 O 5 at different temperatures.

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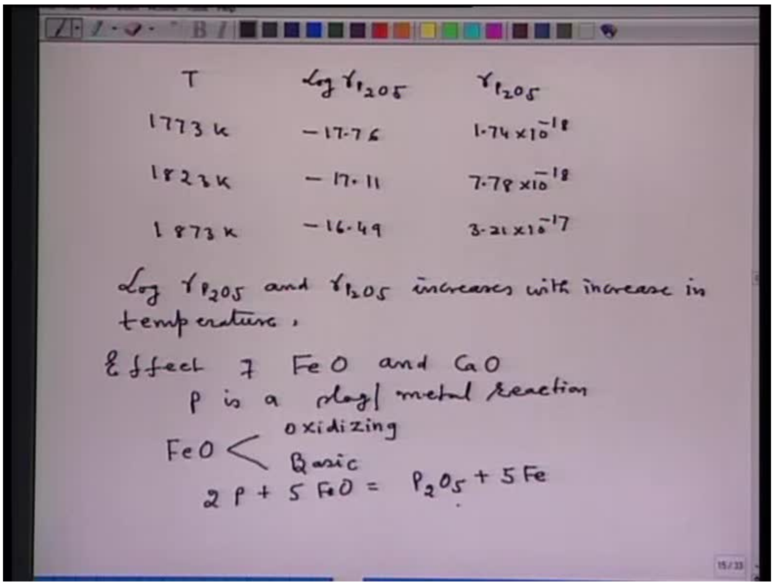

T	$\log \gamma_{P_2O_5}$	$\gamma_{P_2O_5}$
1773 K	−17.76	1.74×10^{-18}
1823 K	−17.11	7.78×10^{-18}
1873 K	−16.49	3.21×10^{-17}

$\log \gamma_{P_2O_5}$ and $\gamma_{P_2O_5}$ increases with increase in temperature.

Effect of FeO and CaO

P is a slag/ metal reaction

$\mathrm{FeO} <$ oxidizing
Basic

$2P + 5FeO = P_2O_5 + 5Fe$

So, for example, I take here temperature, I take here log gamma P 2 O 5 and I calculate here gamma P 2 O 5. I take 3 temperatures 1773 Kelvin, 1823 Kelvin and 1873 Kelvin. I calculate log gamma P 2 O 5 minus 17.76, minus 17.11, minus 16.49, gamma P 2 O 5 is 1.74 into 10 to the power minus 18, and 78 into 10 to the power minus 18 and 3.21 into 10 to the power minus 17. Now, what is the conclusion?

Conclusion is that log gamma P 2 O 5 and hence gamma P 2 O 5 increases with increase in temperature, with increase in temperature.

So, what does it follow from here, that low temperature favors dephosphorization. As I have said many times, that the low temperature favors the dephosphorization and the calculation also shows, because one of the essential condition for dephosphorization is drastically reduce activity of P 2 O 5. So, the low temperature favors the dephosphorization.

Now, let us show the effect of Fe O and Ca O. What is the effect of Fe O and Ca O on dephosphorization?

Now, remember phosphorous is a slag metal reaction. Now, with this I mean that, the removal of phosphorous required the presence of slag, number 1. Number 2, slag should also provide enough amount of oxygen for the reaction phosphorous to convert to P 2 O 5. So, that is why it is called as a slag metal reaction.

Now, as regards the nature of Fe O, Fe O in fact, it can provide oxygen for the reaction, that means it can maintain oxidizing atmosphere. It is also basic in nature. However, it is weak base as compared to, for example, calcium oxide.

So, in its role of oxidizing atmosphere, we can write down the reaction say 2 P plus 5 Fe O, that is equal to P 2 O 5 plus 5 iron. So, in this reaction Fe O is providing oxygen to react with phosphorous and to get P 2 O 5.

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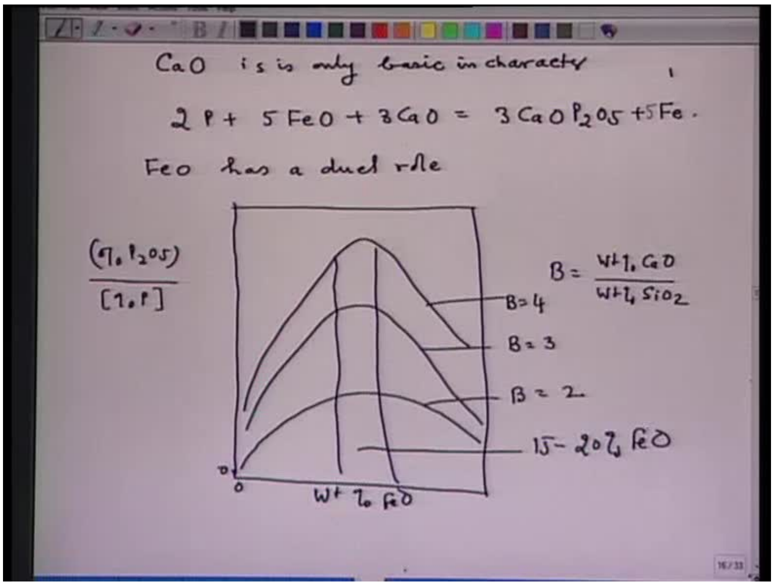

CaO is is only basic in character

$$2P + 5FeO + 3CaO = 3CaO\,P_2O_5 + 5Fe.$$

FeO has a duel role

Now, as regards calcium oxide, calcium oxide cannot provide oxygen for reaction with phosphorous. So, calcium oxide, it is only basic in character. Now, from the definition of basicity, it is the number of oxygen ions that calcium oxide can provide, oxygen ions for the requirement of the reaction.

Another important feature, calcium oxide is a stronger base as compared to Fe O. So, if we write down the reaction, now total reaction 2 P plus 5 Fe O plus 3 Ca O, that would be equal to 3 Ca O P 2 O 5 plus 5 iron.

Now, in this particular reaction, Fe O, though it supplies oxygen for reaction with phosphorous, but, it also plays the role of basicity. So, that means Fe O has a dual role. Fe O has a dual role as I will, already I had pointed out, oxidizing as well as basic, but, weaker basic than calcium oxide. So, if any point of time of the reaction, if Fe O replaces calcium oxide, then the dephosphorization will decrease, because Fe O is a weaker base than calcium oxide. Now, this effect is illustrated in the following figure.

So, if I plot now here, if I plot weight percent Fe O against percentage P 2 O 5 in slag upon percentage phosphorous in metal, that is the dephosphorization or index of dephosphorization or coefficient of partition of phosphorous between slag and metal, whichever way you want to call, what I am plotting, I am plotting dephosphorization index as a function of weight percent Fe O. Of course, here is 0, here it is 0, as a function of basicity. So, basicity is defined here as B, that is equal to weight percent Ca O upon weight percent Si O 2.

So, if I plot now, for different B or basicity ratios, so they are, say for example, B that is equal to 2 , this is for example, B is equal to 3 and this is for example, B is equal to, for example, 4.

Now, what this particular presentation indicates? First it indicates that, as weight percent Fe O increases, the dephosphorization index, it increases, reaches up to a maximum value and after the maximum value, further increase in Fe O, it decreases the dephosphorization index.

Now, this particular observation is valid for all basicities of slag. Now, what does that mean? That means, if we consider for example, a nature of variation for basicity equal to 4, as you increase the weight percent of Fe O, the initial increase of dephosphorization up to a certain optimum value of Fe O and then it further decreases, after reaching the optimum value with the increase in the Fe O content of the slag.

Now, initial increase is because of the oxidizing effect of Fe O. After reaching the maximum value, the concentration of Fe O or the percentage of Fe O in the slag increases. On account of this, the Fe O begins to replace calcium oxide and Fe O is a weak base as compared to calcium oxide. Therefore, the dephosphorization again decreases beyond certain optimum value of percentage of Fe O. That means Fe O is a dual role, one is the oxidizing and in the decreasing mode, where dephosphorization decreases, Fe O, it dilutes the effect of calcium oxide.

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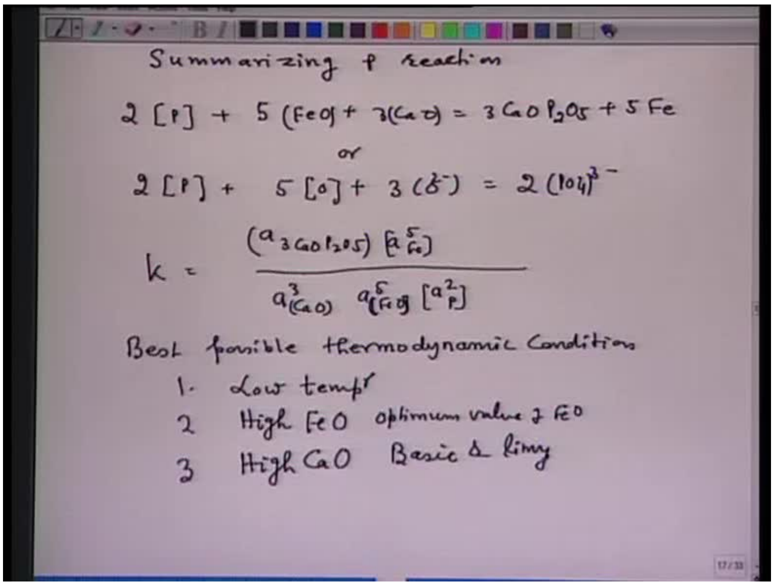

Summarizing P reaction

$$2[P] + 5(FeO) + 3(CaO) = 3CaO\,P_2O_5 + 5Fe$$

or

$$2[P] + 5[O] + 3(O^{2-}) = 2(PO_4)^{3-}$$

$$k = \frac{(a_{3CaO\,P_2O_5})\,[a^5_{Fe}]}{a^3_{(CaO)}\; a^5_{(FeO)}\,[a^2_P]}$$

Best possible thermodynamic Conditions

1. Low tempr
2. High FeO optimum value of FeO
3. High CaO Basic & limy

So, in fact this optimum Fe O, this optimum Fe O is around 15 to 20 percent of Fe O. So, that is what about the effect of Fe O and Ca O. Now, summarizing this, now, summarizing the phosphorous reaction, you can write down 2 P plus 5 Fe O plus 3 Ca O, that is equal to 3 Ca O P 2 O 5 plus 5 iron or in the ionic form, we can also put it, 2 P plus 5 O plus 3 O 2 minus that is equal to 2 P O 4 3 minus.

So, if I write down the value of K, K will be equal to activity 3 Ca O P 2 O 5 plus activity of iron to the power 5 upon activity cube of calcium oxide upon activity 5 Fe O upon activity square upon phosphorous. Now, this is in the slag, this is in the metal, this is in the slag, this is in the metal and this is in the slag.

Now, from here we can arrive at best possible thermodynamic conditions for phosphorous removal. Number 1, as I will illustrated, low temperature. Number 2, high

Fe O, but, optimum, optimum value of Fe O, up to 15 to 20 percent and third, high calcium oxide, that means slag should be basic and limy.

Now, here it is important that Fe O should be dissolved in slag. It should not be undissolved. Kinetically, stirring is always better for enhancing the rate of slag metal reaction.

Now, just I have to tell little bit about the condition for simultaneous removal of carbon and phosphorous. Now, you know, that from the point of view of a steel making, hot metal contains silicon, carbon, manganese, phosphorous.

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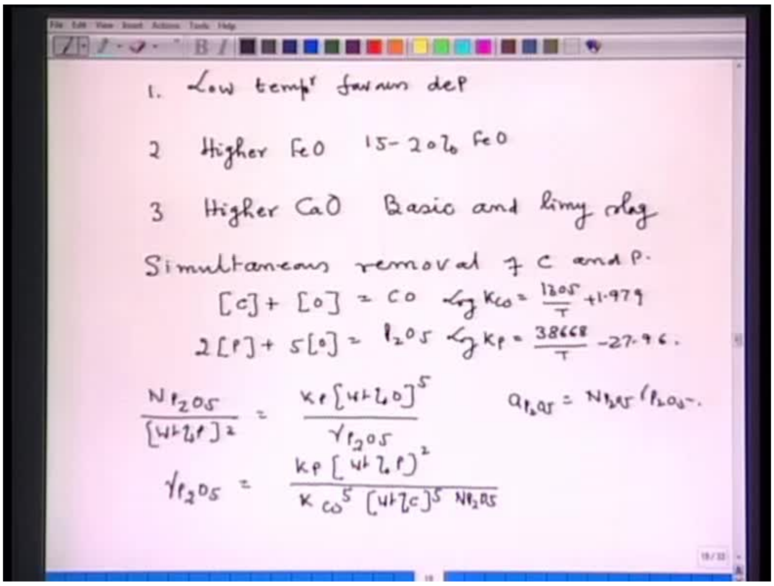

1. Low tempr favours dep

2 Higher FeO 15-20% FeO

3 Higher CaO Basic and limy slag

Simultaneous removal of C and P.

$$[C] + [O] = CO \quad \log K_{CO} = \frac{1305}{T} + 1.979$$

$$2[P] + 5[O] = P_2O_5 \quad \log K_P = \frac{38668}{T} - 27.96.$$

$$\frac{N_{P_2O_5}}{[wt\%P]^2} = \frac{K_P[wt\%O]^5}{\gamma_{P_2O_5}} \qquad a_{P_2O_5} = N_{P_2O_5}\gamma_{P_2O_5}.$$

$$\gamma_{P_2O_5} = \frac{K_P[wt\%P]^2}{K_{CO}^5[wt\%C]^5 N_{P_2O_5}}$$

You have also noted that, the silicon and manganese, they are removed comparatively very very fast. It is only carbon and phosphorous that require little more time. So, let us see the simultaneous removal of carbon and phosphorous. I will initiate, then you complete it and let us see. Simultaneous removal of carbon and phosphorous. For that, we write down the reaction, C plus O that is equal to CO. Let us put it log of K CO 1305 upon T plus 1.979. Then, I will write down 2 P plus 5 O, that is equal to P 2 O 5 and log of K P, that is equal to 38668 upon T minus 27.96.

Now, I can write down the value of K P. I can write down the value K CO and I substitute them in order to get this equation. This you can do yourself. You write down the value of K CO. You write down the value of K P, and then, get the following equation, N P 2 O 5 upon weight percent P whole square, that is equal to K P into weight percent O to the power 5 upon gamma P 2 O 5. Now, note, you have to use also, activity of P 2 O 5, that is equal to N P 2 O 5 into gamma P 2 O 5.

Now, I have to replace weight percent O also. Already, I have given the equations. So, if I do that and if I substitute that value of weight percent O over here, and I try to get this equation gamma P 2 O 5, that will be equal to K P into weight percent P whole square upon K CO to the power 5 weight percent carbon to the power 5 N P 2 O 5. So, for the simultaneous removal of carbon and phosphorous, the value of gamma P 2 O 5 calculated from this equation is required.

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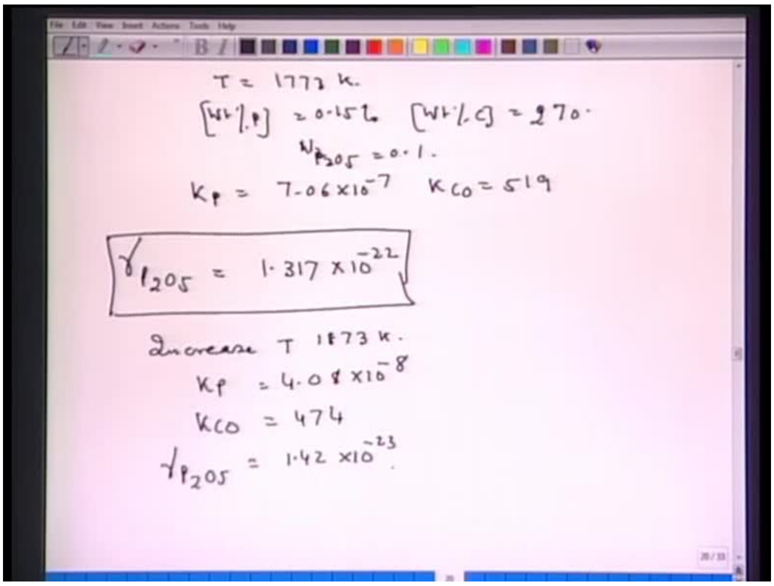

$T = 1773\ K.$

$[wt\%P] = 0.15\%$ $[wt\%C] = 2\%.$

$N_{P_2O_5} = 0.1.$

$K_P = 7.06 \times 10^{-7}$ $K_{CO} = 519$

$$\boxed{\gamma_{P_2O_5} = 1.317 \times 10^{-22}}$$

Increase T $1873\ K.$

$K_P = 4.08 \times 10^{-8}$

$K_{CO} = 474$

$\gamma_{P_2O_5} = 1.42 \times 10^{-23}.$

Now, let us do some simple calculation. Say, I take temperature equal to 1773 Kelvin. I take say, weight percent phosphorous, let us take 0.15 percent, weight percent carbon in metal, let me take 2 percent, N P 2 O 5 let me take 0.1, then I can calculate the value of K P, that is equal to 7.06 into 10 to the power minus 7. I calculate value of K CO 519.

Now, I substitute all these values into this, say gamma P 2 O 5. If I substitute all these values, then I will be getting gamma P 2 O 5 equal to 1.317 into 10 to the power minus 22.

What this suggests? Simultaneous removal of carbon and phosphorous is possible. It is possible only when the activity of P 2 O 5 is drastically reduced. Then a carbon reaction and phosphorous reaction can take place together.

Now, I here itself I can illustrate, what will happen if I increase the temperature. Now, suppose if I increase temperature to 1873 Kelvin, then K P that is equal to 4.08 into 10 to the power minus 8, K CO that is equal to 474 and then the gamma P 2 O 5, which I will require that is equal to 1.42 into 10 to the power minus 23.

That is, if you go for a little higher temperature, phosphorous reaction may occur, but, then you will still require a very large reduction in the value of gamma P 2 O 5. Therefore, for the simultaneous removal of carbon and phosphorous, one has to see a slag which has a very low value of gamma P 2 O 5 is formed and then carbon and phosphorous reaction may be allowed to take place simultaneously, such that the carbon removal is slightly delayed as compared to the phosphorous removal.

So, that point we should remember. I will be needing it, when we will go in the modern is steel making practice. Now, I will give you the references and the questions for self-assessment.

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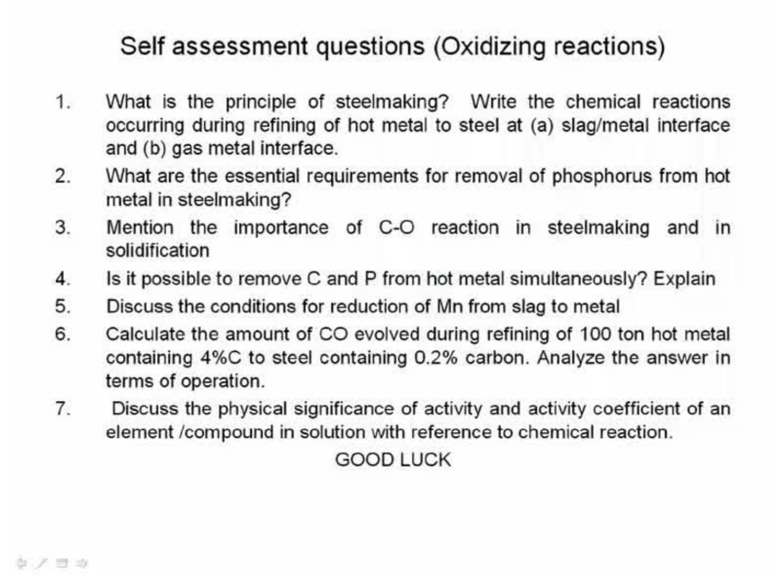

Self assessment questions (Oxidizing reactions)

1. What is the principle of steelmaking? Write the chemical reactions occurring during refining of hot metal to steel at (a) slag/metal interface and (b) gas metal interface.
2. What are the essential requirements for removal of phosphorus from hot metal in steelmaking?
3. Mention the importance of C-O reaction in steelmaking and in solidification
4. Is it possible to remove C and P from hot metal simultaneously? Explain
5. Discuss the conditions for reduction of Mn from slag to metal
6. Calculate the amount of CO evolved during refining of 100 ton hot metal containing 4%C to steel containing 0.2% carbon. Analyze the answer in terms of operation.
7. Discuss the physical significance of activity and activity coefficient of an element /compound in solution with reference to chemical reaction.

GOOD LUCK

Now, here are the some questions for your self-assessment on the oxidizing reactions. What is the principle of steel making? Write the chemical reactions occurring during refining of hot metal to steel at slag metal interface and gas metal interface, already I have given.

Second, what are the essential requirements for removal of phosphorous from hot metal in steel making? Right now we have discussed.

Mention the importance of CO reaction steel making and in solidification. Both things I have discussed, one way is provide good agitation and it provides a rimming reaction during solidification.

Is it possible to remove carbon and phosphorous from hot metal simultaneously? Explain. Just now I have discussed in brief. It is towards the end of the lecture. I will request you to write down the equilibrium values, to calculate and get a feel, that the simultaneous removal of carbon and phosphorous is possible, only when the activity of P 2 O 5 is drastically reduced and that is the secret of success of modern steel making practice.

Discuss the conditions for reduction of manganese from slag to metal. Calculate the amount of CO evolved during refining of 100 ton hot metal containing 4 percent carbon to steel containing point 2 percent carbon. Analyze the answer in terms of operation. Now, all that I wanted you to understand, how much amount of CO will be evolved and what is the implication in terms of foaming of the slag, in terms of easy escaping tendency from the atmosphere.

7, discuss the physical significance of activity and activity coefficient of an element or compound in solution with reference to chemical reaction. Only thing I want to you to stress, to know the physical meaning of activity, anything which is free it is highly active, anything which is not free is not active and hence its activity will be reduced. So, it is in that term, you have to understand activity and activity coefficient. See I wrote here, good luck.

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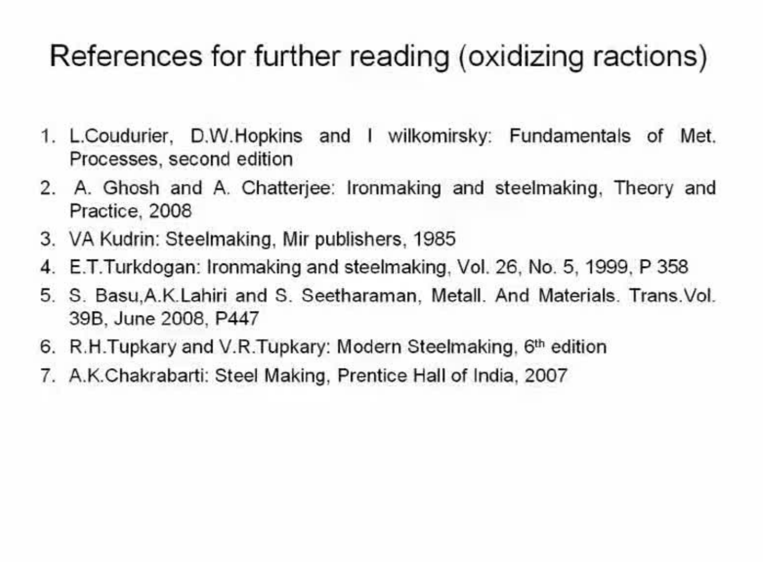

References for further reading (oxidizing ractions)

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Now these are the references for further reading.