Steel Making

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Module No. # 01
Lecture No. # 10
Modern Steelmaking I, Oxygen Steelmaking

We were discussing steel making fundamentals and in the last lecture, I have given you slag making and there I have said that make a slag and slag will make your steel. So, we have seen the fundamental considerations of slag making and we have understood the requirements of slag for the purpose of refining of steel.

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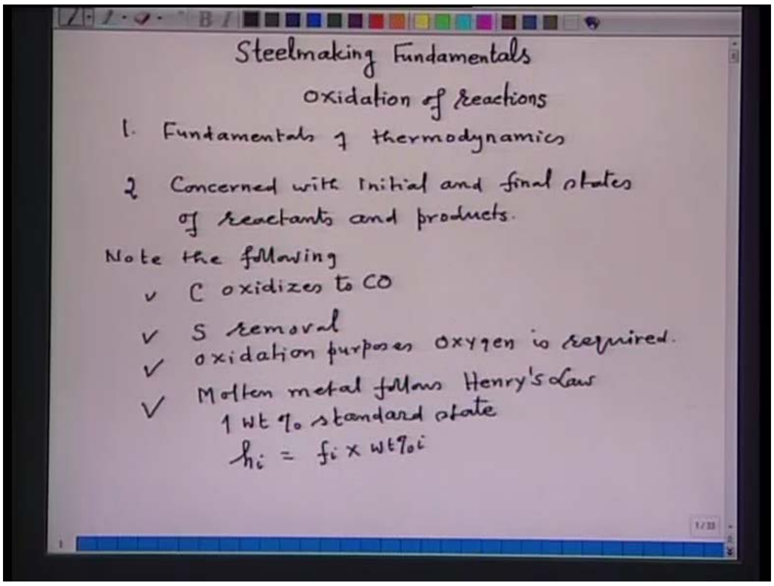

Steelmaking Fundamentals

Oxidation of Reactions

1. Fundamentals of thermodynamics

2 Concerned with Initial and final states of reactants and products.

Note the following
- ✓ C oxidizes to CO
- ✓ S removal
- ✓ oxidation purposes oxygen is required.
- ✓ Molten metal follows Henry's Law
  1 wt % standard state
  $h_i = f_i \times wt\%_i$

Now, another steel making fundamental, corresponds to oxidation of reactions. In fact, if you recall, the definition of steel making, there I have said that steel making involves removal of impurities through oxidation and slag formation.

So, next, steel making fundamental comprises of the various oxidizing reactions or so called oxidation of reaction. Now, hot metal - it contains carbon, sulphur, phosphorous, silicon and manganese. In order to remove these impurities, we have to provide an oxidation atmosphere or I can say that we have to blow oxygen.

So, before we apply the fundamental consideration for oxidation purposes, I would like to tell you few notes. Number 1: say, we will be using fundamentals of thermodynamics in exploring the optimum conditions that are required for removal of an impurity. Now, when I say fundamentals of thermodynamics, we will be concerned with equilibrium thermo dynamics and solution thermodynamics and with that the equilibrium constant of a reaction and the solution thermodynamics we will be mainly concerned with.

In doing so, that is in applying these fundamentals of thermodynamics, what we will be doing? We will be concerned with initial and final states of reactants and products.

To illustrate this, suppose, we take the reaction silicon plus 2 O is equal to SiO 2, then we will be considering the silicon and oxygen is the initial stage and SiO 2 is the final stage. So, in arriving at the final stage, what are the optimum conditions that will be necessary and that we will try to achieve by the use of equilibrium and solution thermodynamics. Now, in this attempt, please note the following.

Point number 1: we will consider carbon oxidizes to carbon monoxide. Now, in fact, you may recall that carbon oxidizes to CO and CO 2, but the temperature involved in steel making is very high of the order of 1400, 1500 or 1600 Celsius. So, the probability of formation of CO 2 is very low and hence, in all our thermodynamic assessment of refining reaction as far as carbon is concerned, we will be writing carbon plus O is equal to CO; that means, the principle gaseous product of carbon reaction is carbon monoxide.

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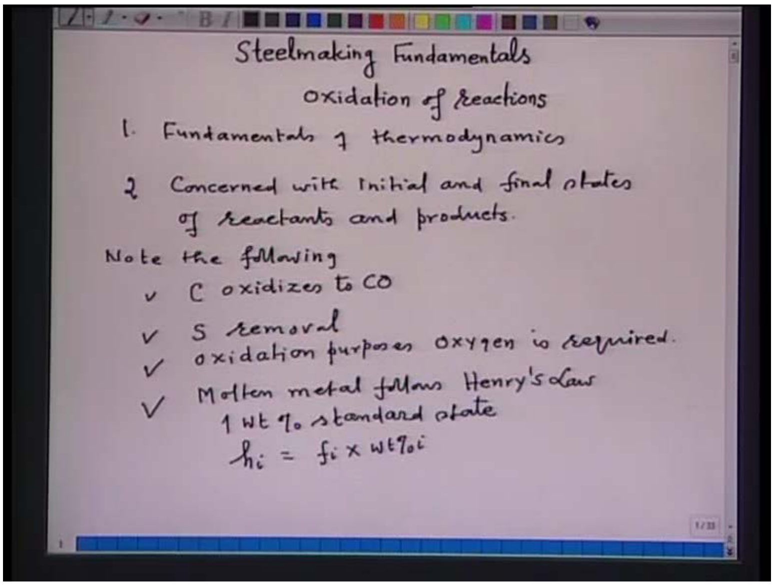

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Number 2: sulphur removal occurs under reducing slag meaning thereby, that in an oxidizing atmosphere though removal of sulphur occurs, it occurs to a very minimum extent. The ideal location for removal of sulphur is blast furnace because in the blast furnace, highly reducing conditions are there. Most of the sulphur is eliminated in the hot metal formation stage. So, in our thermodynamic assessment, we will not be considering the removal of sulphur on the pretext that steel making is done under oxidizing atmosphere, little amount of sulphur can be removed as SO 2, but the probability of that removal is very small. So, in our thermo dynamic assessment, we will not be considering removal of sulphur during steel making.

Number 3: for oxidation purposes, oxygen is required; that means, we have to blow oxygen. The chance of reaction between the impurity elements and the gaseous oxygen is considered to be negligibly small. With that what I mean is that, the oxidation reaction will occur only when oxygen is dissolved in the hot metal.

That means, the oxidizing reaction will comprise of the element or the impurity in hot metal and oxygen dissolved in hot metal. Other way round, the chance or the probability of reaction of an impurity with the gaseous oxygen is negligibly small and in our thermodynamic assessment, we will not be considering the reaction between impurity of an element and the gaseous part of the oxygen.

Number 4: from the thermodynamic consideration, when we want to write down the equilibrium constant, then we require the activity of the elements.

Now, since the concentration of impurity in hot metal and steel is below 1 weight percent, though carbon is 4 weight percent, but during removal it goes down to 1 percent. So, in all our thermodynamic assessment, we will consider the molten metal follows Henry’s law, since molten metal is a dilute solution of impurity element.

So, we are very safe in assuming that the elements in the molten metal or steel, they follow the Route’s law and we will also take 1 weight percent as the standard state. We will also assume 1 weight percent standard state. Pure element is also the standard state for example, in case of Routes law. 1 weight percent is the standard state, when the impurity elements, they are below 1 weight percent.

So, as such, we will be using 1 weight percent as the standard state and we denote the activity of elements in molten metal or steel by Henrian activity and as such, the relation h i that is equal to f i into weight percent i, i is the element which is under consideration. So, following this we will use now, the thermodynamics.

Now, what happens? Suppose, when oxygen is blown then oxidation of impurities including iron occur simultaneously. It is not that when we blow oxygen only selectively iron or selectively carbon or selectively silicon or selectively manganese or selectively phosphorous will oxidize, but they will all occur simultaneously.

In fact, there is a competition between the element and the oxygen. The reaction, which has the maximum negative free inner deformation though will occur first, but the probability of simultaneously occurrence of oxidation of all impurities cannot be overruled, but then considering this fact that all the impurities occur simultaneously, it is not possible for us to arrive at the optimum conditions for the removal of impurity.

So, in our subsequent treatment on thermo dynamic assessment, what we will be considering is the equilibrium between an element and the oxygen. Other way round, I will be considering only one impurity at a time that means oxidation of n impurity occurs at one time; all others will occur not at that particular time.

So, now if you do that, we have to consider all impurities one by one and we will try to arrive at the optimum thermodynamic condition for their removal.

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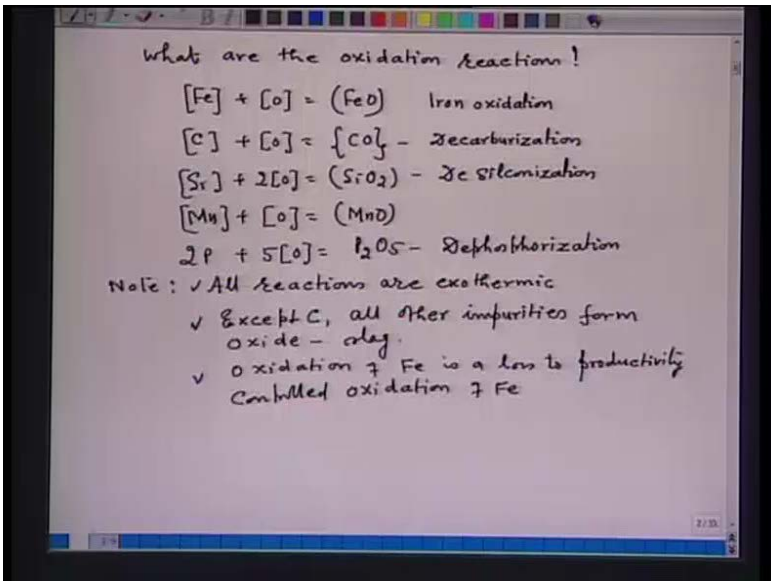

What are the oxidation reactions ?

$[Fe] + [O] = (FeO)$ Iron oxidation

$[C] + [O] = \{CO\}$ – Decarburization

$[Si] + 2[O] = (SiO_2)$ – De silconization

$[Mn] + [O] = (MnO)$

$2P + 5[O] = P_2O_5$ – Dephosphorization

Note : ✓ All reactions are exothermic

✓ Except C, all other impurities form oxide – slag.

✓ oxidation of Fe is a loss to productivity
Controlled oxidation of Fe

Now, under this constraint, we can write down the oxidation reactions. In fact, you will be wondering what the oxidation reactions are. I will write down all the reactions: iron in metal plus O in metal that is, equal to FeO in slag; similarly, carbon plus O, that is, CO and this reaction is called decarburization, a very important reaction in steel making; this reaction is called iron oxidation. Also very important, as you recall, in the definition of steel making I have said that the depth steel should have minimum oxygen content and slag should have minimum iron content.

Therefore, oxidation of iron is also a very important reaction. Similarly, silicon plus 2 O, it gives SiO 2; this reaction is called de-silconization. Similarly, manganese plus O, MnO, 2P plus 5 O, that is equal to P 2 O 5 and this reaction is de-phosphorization. Note down few important facts: first, all reactions are exothermic in nature; one particular important thing.

Second important thing: except carbon, which is removed as gaseous phase, all other impurities form oxide and as we know from our earlier lecture, they are called slag; they form a slag.

So, now you can note that slag is a very important part of steel making. So, in my last lecture, when I was said that make a slag; slag will make your steel. Now, you understand why slag is so important.

Third thing is that oxidation of iron is a loss to productivity. It is in fact, the techno economic parameter of steel making is loss of iron in slag and presence of dissolved oxygen in steel at turn down; these are the 2 techno indices of any steel making process.

Therefore, oxidation of iron should be controlled; therefore, controlled oxidation of iron is required.

Now, why I am telling is this because if you have 100 atoms of hot metal, the impurities altogether, they count around 6 or 7 atoms. So, statistically when we supply oxygen, there are more chances of iron to oxidize then those of the impurities. That is where challenge is there to control the oxidation of iron.

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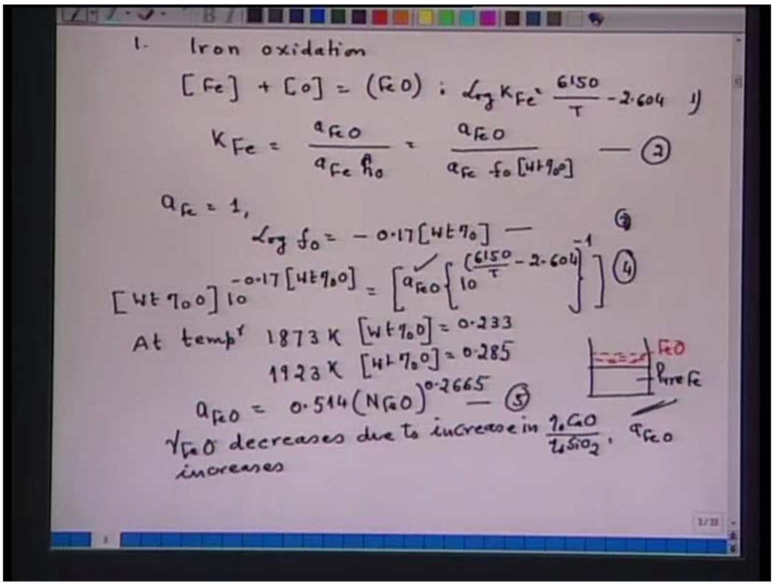

1. Iron oxidation

$[Fe] + [O] = (FeO)$; $\log K_{Fe} = \frac{6150}{T} - 2.604$ 1)

$K_{Fe} = \frac{a_{FeO}}{a_{Fe}\, h_O} = \frac{a_{FeO}}{a_{Fe}\, f_O\, [wt\%O]}$ — ②

$a_{Fe} = 1,$

$\log f_O = -0.17[wt\%]$ — ③

$[wt\%O]\, 10^{-0.17[wt\%O]} = \left[a_{FeO}\left\{10^{\left(\frac{6150}{T} - 2.604\right)}\right\}^{-1}\right]$ ④

At temp^r 1873 K $[wt\%O] = 0.233$

1923 K $[wt\%O] = 0.285$

$a_{FeO} = 0.514 (N_{FeO})^{0.2665}$ — ⑤

γ_{FeO} decreases due to increase in $\frac{\%CaO}{\%SiO_2}$, a_{FeO} increases

Now, with this background I will consider first of all iron oxidation. Iron oxidation can be represented by Fe plus O that is equal to FeO. Log of K iron is equal to 6150 upon T minus 2.604; let me call equation number 1.

Now, here T is in kelvin. If I write down the value of K, so, K iron will be equal to activity of FeO upon activity of iron into Henrian activity of oxygen because we will assume that the elements in molten steel follows the Henrian law.

So, that will be equal to activity of FeO upon activity of iron into f o into weight percent of oxygen. So, let us say this is equation number 2. Now, since iron in steel is pure, we can take activity of iron is equal to 1.

So activity of iron, since it is pure, we take it equal to 1 and f o which is the activity coefficient of oxygen, we will relate with the following equation. Say, log f o that is equal to minus 0.17 into weight percent O; let it be equation number 3.

Now, say by equation 1, 2 and 3, we obtain the following equation. Say, weight percent O 10 raise to the power minus 0.17 weight percent O that is equal to activity of FeO 10 raise to the power 6150 upon T minus 2.604 to the power minus 1, bracket close and let us say this is our equation 4.

So, with the help of this equation 4, for a given temperature T and for a given activity of FeO, one can find out the weight percent oxygen that is dissolved in steel; of course, that oxygen will be the saturated one; that is, the maximum oxygen that will be dissolving at that particular temperature and for that activity of FeO.

So, for example, if you consider a situation, say this is the pure iron, mind you, we are considering iron oxygen equilibrium and no other element is present. So, pure iron, if it is in contact with pure FeO, this is FeO then activity of FeO will be equal to 1.

So, in that case, if we take for example, a temperature, if we take 1873 kelvin and we take another temperature 1923 kelvin and we solve this equation 4, by taking activity of FeO is equal to 1 and taking this particular system under consideration, then we get at 1873 weight percent oxygen, mind you, this is a saturated oxygen, the maximum oxygen that will be equal to 0.233; at 1923 kelvin, the weight percent O, that is equal to 0.285.

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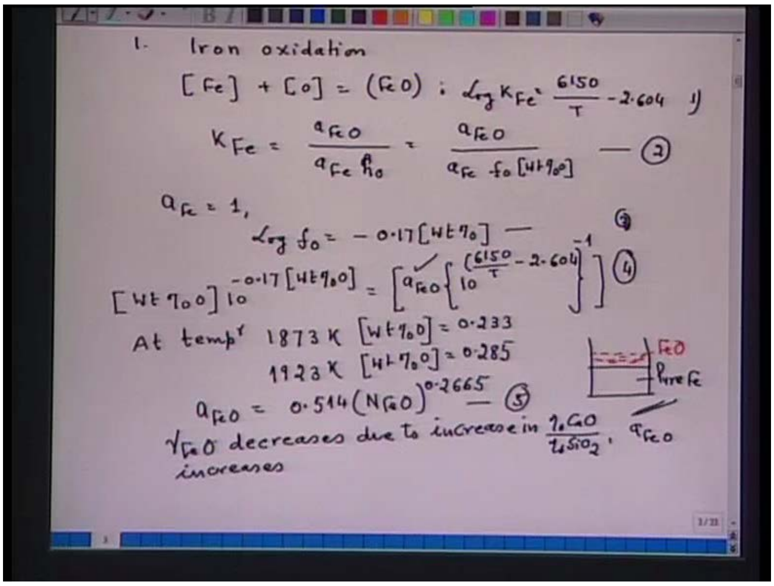

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$[wt\%O] 10^{-0.17[wt\%O]} = \left[a_{FeO}\left\{10^{\left(\frac{6150}{T} - 2.604\right)}\right\}^{-1}\right]$ ④

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γ_{FeO} decreases due to increase in $\frac{\%CaO}{\%SiO_2}$, a_{FeO} increases

So, what we note from here is that increasing temperature increases the oxygen dissolved in iron in a system, when iron is in contact with oxygen. Now, in fact, if you see equation 4, you note that the weight percent oxygen which is dissolved in steel also depends upon activity of FeO.

Now, here we have took activity of FeO is equal to 1. Now, say activity of FeO, you recall that in slag making we have derived one equation, which says that activity of FeO we got that is equal to 0.514 N FeO raise to the power 0.2665; let this equation number 5. There we have said that as gamma FeO decreases, you recall, as gamma FeO decreases due to increase in basicity, due to increase in ratio of percent CaO upon percentage SiO 2, activity of FeO increases.

Now, it is also clear that as gamma FeO decreases that means, more FeO will be available freely and hence, by the concept of activity because activity is a free concentration of that compound or of that element. So, if more amount of FeO is free that is, it is not combined with any oxide, then it can take part in any reaction because the oxide which is combined, cannot take part in that reaction. So, if we increase the basicity of slag as I explained earlier, by adding more amounts of calcium oxide and calcium oxide will react with SiO 2 and FeO gets free and that is why, the activity of FeO increases and that is what, we obtained in our last lecture on slag making.

So, from this relation, we can find out the activity of FeO and we can substitute in equation 4 and we can get what will be the weight percent oxygen, when FeO is not free; that means, in steel making slag, FeO is not generally free. It depends upon the concentration FeO, the concentration of calcium oxide and concentration of SiO 2.

In the beginning, FeO and SiO 2 react together in the absence of calcium oxide. So, the reactivity of FeO is very low. If we add calcium oxide, then the calcium oxide reacts with SiO 2 and FeO gets free. So, the activity of FeO increases. What I mean to say in a solution, there are different oxides present; activity of FeO may not be necessarily equal to 1. In fact, it is not equal to 1. Let us see the effect of slag

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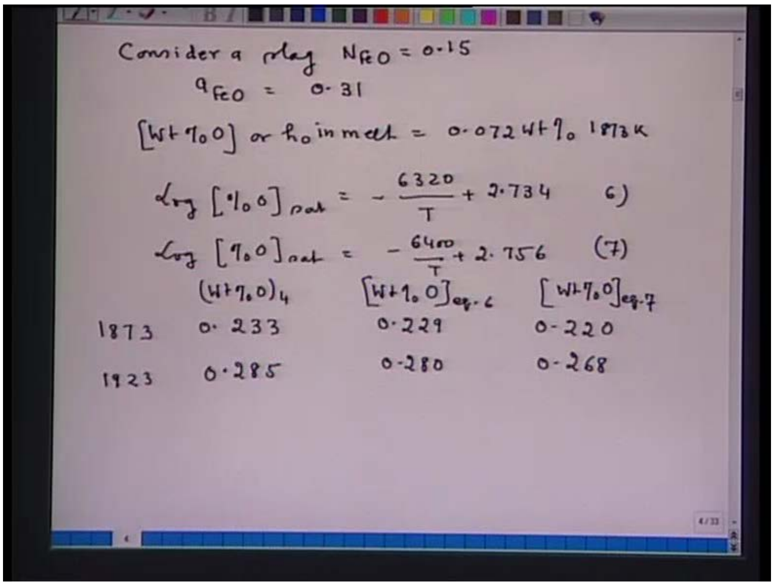

Consider a slag $N_{FeO} = 0.15$

$a_{FeO} = 0.31$

$[Wt\ \%\ O]$ or h_O in melt $= 0.072$ wt % 1873 K

$$\log\,[\%O]_{sat} = -\frac{6320}{T} + 2.734 \quad 6)$$

$$\log\,[\%O]_{sat} = -\frac{6400}{T} + 2.756 \quad (7)$$

	$(Wt\ \%\ O)_4$	$[Wt\ \%\ O]_{eq.6}$	$[Wt\ \%\ O]_{eq.7}$
1873	0.233	0.229	0.220
1923	0.285	0.280	0.268

Now, for example, let us consider slag, whose activity consider a slag, where N FeO that is, equal to 0.15. Now, we can determine the activity of FeO from equation 5 and that comes to be equal to 0.31. The weight percent oxygen or h o in melt, that is, activity of that will be equal to 0.072 weight percent because what you have to do at 1873 kelvin. What you have to do? You have to simply multiply the value of this activity of FeO, 0.31 with this 0.233.

So when you multiply this, then you will be getting 0. 072 weight percent at 1873 kelvin. What it says? The activity of FeO decreases from 1 to 0.31, then the oxygen dissolved in steel also decreases from 0.233 to 0.072 weight percent; that is what, the role of activity of FeO. Now, by telling all these things what I wanted to communicate to you is that the presence of FeO in slag, it determines the oxidation or reduction potential of the slag. If the FeO content of the slag is low, slag is reducing; if the FeO content of slag is high, the slag is oxidizing as I have said earlier also and I want to repeat here also because of its importance.

Now in the literature, other equations are available. For example, in one of the equations says log of percent O at saturation that is equal to minus 6320 upon T plus 2.734; let us call this equation as 6 and log percent O saturate that is equal to minus 6400 T plus 2.756.

Now, the whole idea is that you may come across with the different sources and the value of weight percent oxygen dissolved, it may differ because all that depends upon what parameters we are substituting. There are number of sources and the sources are little bit different, then what value I have calculated, you may not get the same. So, I could come across some other sources and if I calculate now, if I put say, 1873 and 1923, I calculate weight percent O from equation 4, weight percent O from equation 6 and weight percent O from equation 7. In all the cases, I assume activity of FeO is equal to 1. For any other activity of FeO, that value can be multiplied by that value of activity and you get the oxygen dissolved for that activity and at that particular temperature.

So, if I use equation four, already we have determined 0.233, 0.285, 0.229, 0.280, 0.220 and 0.268. Note that there is a slight difference in the values of weight percent oxygen that is dissolved in the steel by using the different sources, but all these sources they appear to say that increase in temperature increases the dissolved oxygen in steel and that is what is an important conclusion for this particular iron oxidation reaction.

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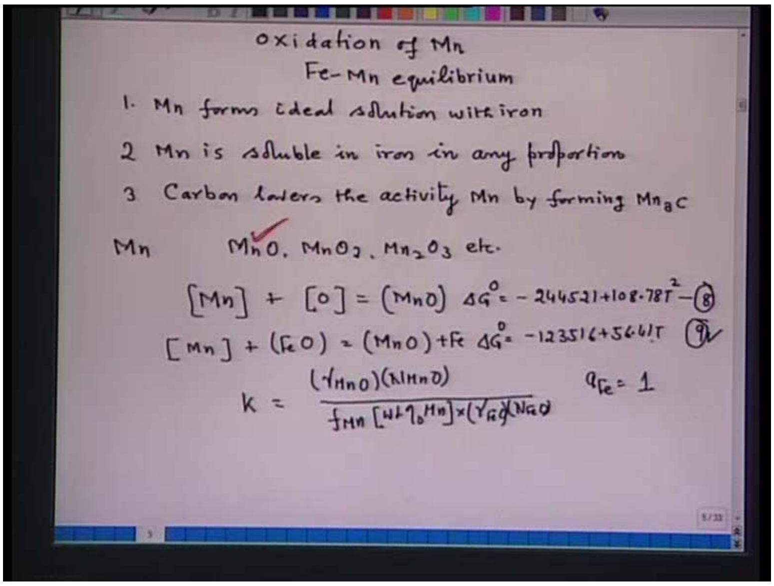

oxidation of Mn

Fe-Mn equilibrium

1. Mn forms ideal solution with iron
2. Mn is soluble in iron in any proportion
3. Carbon lowers the activity Mn by forming Mn_3C

Mn MnO, MnO_2, Mn_2O_3 etc.

$$[Mn] + [O] = (MnO) \quad \Delta G^0 = -244521 + 108.78T^2 \quad ⑧$$

$$[Mn] + (FeO) = (MnO) + Fe \quad \Delta G^0 = -123516 + 56.41T \quad ⑨$$

$$K = \frac{(\gamma_{MnO})(N_{MnO})}{f_{Mn}[wt\%Mn] \times (\gamma_{FeO})(N_{FeO})} \qquad a_{Fe} = 1$$

Next, we consider oxidation of manganese. In fact, we are considering iron, manganese equilibrium. We are considering Some point to be noted say, manganese it forms ideal solution with iron; that means, manganese and iron, they do not form any inter metallic compound and that is what the ideal solution means. Second: manganese is soluble in iron in any proportion.

Third: carbon lowers the activity of manganese by forming Mn 3 C is manganese carbide in a system Fe MnC. If it is quite clear, if some part of the manganese forms a compound with any other element, then its activity will be reduced.

Now, say, manganese oxidation is relatively very simple. Manganese oxidation can occur relatively at lower temperature and it can form many oxides. For example, manganese can be oxidized to MnO and also be oxidized to MnO 2, it can also be oxidized to Mn 2 O 3 and other type of oxide, but under steel making condition, the MnO oxide is the most stable and as such, we will consider the oxidation of manganese as MnO. So, we write down the reaction; manganese plus O that is equal to MnO in the slag and the value of delta G naught that is a standard free energy change. Now, these values of standard free energy change are given, when the activity of the respective components are in their own standard state. So, delta G naught for this reaction is minus 244521 plus 108.78 T squared and let us call this reaction is number 8.

Another reaction which is also very important is the oxidation of manganese by FeO content of the slag; that is, the Mn plus FeO that is equal to MnO plus Fe and delta G naught that is equal to minus 123516 plus 56.41 T; this is equation 9.

Now this equation 9, it suggests the oxidation of manganese, but the reverse reaction we can call it to be reduction of manganese. In fact, during steel making, the reduction of manganese is also very important because the oxidation of manganese causes MnO to form and it accumulates in the slag.

So, at some point of time, it is also possible that the MnO may get reduced by the iron and manganese content of the bath also increases. So, the forward reaction in case of equation number 9 is called oxidation and the reverse reaction is called reduction of manganese.

Now, you note also that both these reactions are highly exothermic in nature; that means, reduction of manganese from slag becomes favourable at a rising temperature. Manganese of the slag can be reduced by carbon, iron or silicon; that means, though the reaction 9 we have written, if we consider the reduction of manganese then we use iron as the reducing agent, but in fact carbon or silicon can equally be there which can reduce MnO, but let us consider the equation 9 and we write down the value of K. K, that is equal to gamma MnO into N MnO upon f Mn into weight percent Mn into gamma FeO into N FeO.

Now, here what we have done, we assume activity of iron which is pure that is equal to 1; that is what the one assumption is there. Now, it is already known I believe to all of you that slags are concentrated liquid solutions and the activity of the components in slag, they obey Routes law; their activity is equal to gamma into mole fraction and the molten metal or liquid steel, they are dilute solutions and they obey the Henrian law.

So, accordingly, the term gamma MnO it is the activity coefficient of MnO on the Routian scale and f Mn is the activity coefficient of manganese on the Henrian scale or more precisely, on the 1 weight percent standard state.

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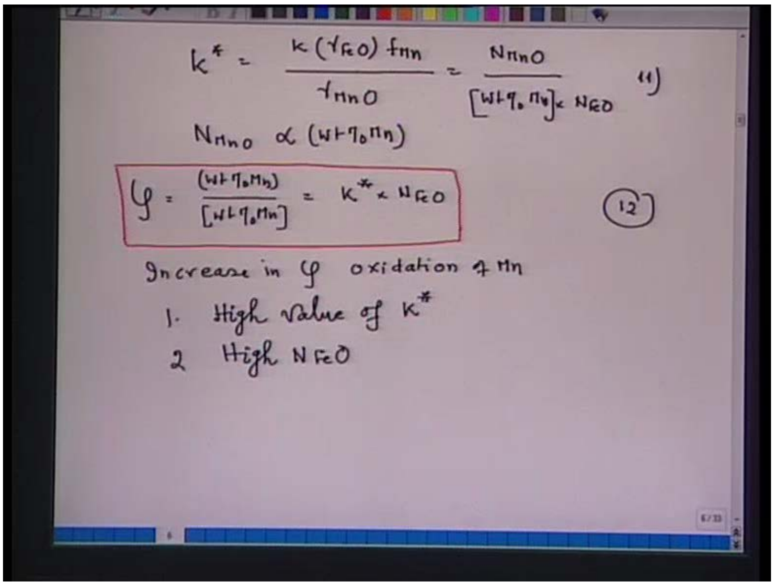

$$k^* = \frac{k(\gamma_{FeO}) f_{Mn}}{\gamma_{MnO}} = \frac{N_{MnO}}{[wt\%Mn] \times N_{FeO}} \quad 11)$$

$$N_{MnO} \propto (wt\%Mn)$$

$$\boxed{\varphi = \frac{(wt\%Mn)}{[wt\%Mn]} = K^* \times N_{FeO}} \quad ⑫$$

Increase in φ oxidation of Mn

1. High value of K^*
2 High N_{FeO}

Now, what we can do? We group all the terms which correspond to the activity coefficient of a component or of an element and then we write down the value as K star that is equal to K gamma FeO f Mn upon gamma MnO that will be equal to N MnO upon weight percent Mn into N FeO and let us call this equation is number 11.

Here, this K star is called as equilibrium quotient. Now, the difference between K, which I have written in the equation number 10 and K star is as follows.

K is an equilibrium constant; K star is an equilibrium quotient. Now, it depends upon the composition of the slag acidic slag or basic slag to the value of K star will be different depending on the type of slag. So, remember that K star, which is the equilibrium quotient, it strongly depends upon the composition of slag. We just write N MnO is approximately proportional to weight percent manganese in slag.

Then we can write down phi, which is the coefficient of distribution of manganese in slag and metal that is, equal to weight percent manganese in slag upon weight percent manganese in metal that comes out to be equal to K star into N FeO.

So, this is a reaction which tells about the distribution coefficient of manganese in iron manganese equilibrium system.

This is equation number 12. Now, from the equation number 12, if we want to oxidize manganese, that means, the value of weight percent manganese upon weight percent manganese should be high.

So, increase in phi or increase in coefficient of distribution of manganese that means, oxidation of manganese is favoured by, if you see this equation, first, high value of K star and second, high N FeO. So, these two conditions they will lead you to oxidation of manganese.

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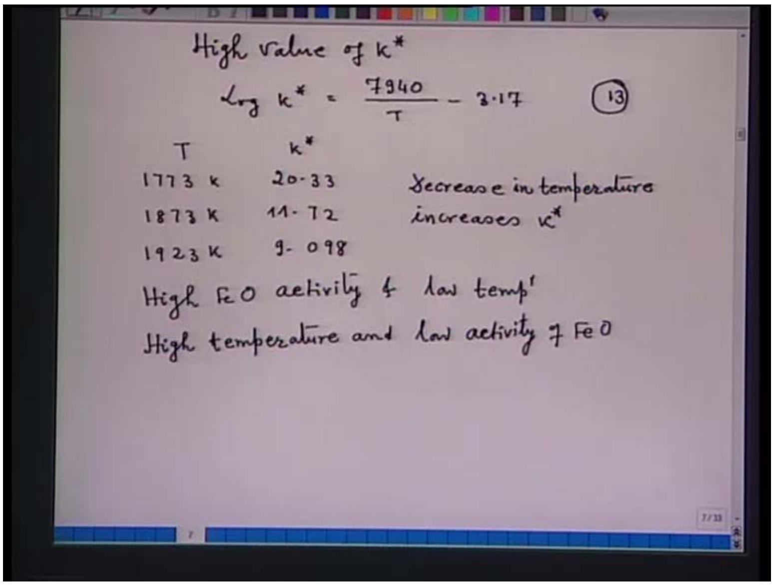

High value of k^*

$$\log k^* = \frac{7940}{T} - 3.17 \quad (13)$$

T	k^*
1773 K	20.33
1873 K	11.72
1923 K	9.098

Decrease in temperature increases k^*

High FeO activity & low temp'

High temperature and low activity of FeO

Now, how to obtain high value of K star? First condition: high value of K star because just alone telling that high value of K star will give you high ratio of the coefficient of distribution. Then, we have to say also how to obtain. As I have said that the K star depends upon composition of slag as well as on the temperature also. As regards the temperature, we can write down this equation log K star that is equal to 7940 upon T minus 3.17 and I write this equation as number 13.

Let us calculate and see what is the effect of temperature because you want high value of K star remember. So, that temperature which gives high value of K star will favour the oxidation of manganese.

Let us calculate the value of K star at various temperatures. I take for example, temperature here and K star over there.

So, I take temperature 1773 kelvin, 1873 kelvin and 1923 kelvin. I calculate the value of K star, it comes here 20.33, 11.72 and 9.098. What does it say?

It says that increase in temperature decreases the value of K star, but other way around decrease in temperature increases the value K star. We can write down decrease in temperature increases value of K star that means, oxidation of manganese is favoured by low temperature. So, our earlier statement that we have said that high value of K star is required.

Now, we can transfer this knowledge in terms of knowhow for controlling oxidation of manganese and in that we will provide low temperature because that will favour the oxidation of manganese.

So, that is what the role of temperature is. Another thing is that we said high mole section on N FeO. So, high FeO activity will also favour the oxidation of manganese. Now, high FeO activity means, if FeO and SiO 2 form a compound then the activity of FeO will be low.

If we add calcium oxide into this, then calcium oxide will combine with SiO 2 and FeO will free.

That way one can increase the activity of FeO. So, for manganese oxidation, High FeO activity and low temperature favour the oxidation of manganese. On the contrary, high temperature and low activity of FeO will favour the reduction of manganese from slag. I repeat once again high temperature and low activity of FeO will favour reduction of manganese from slag and manganese concentration in metal increases.

Now, lowered activity of FeO that means the FeO is in combined form or the formation of FeO is less and in both the cases, the manganese reduction of slag is favoured.

A basic slag also favours the reduction of manganese. Remember, this is a very important conclusion from the point of view of production of steel, when we will go to the practice. There we will be using the concept of oxidation and reduction of manganese.

At any point of time, when the activity of FeO is decreased or the temperature becomes high then manganese content of the bath, it will increase. Remember, this will be used when I will go for the practice in my subsequent lecture.

It is a very important conclusion and that I will need at that point of time. Now, I will illustrate with a problem.

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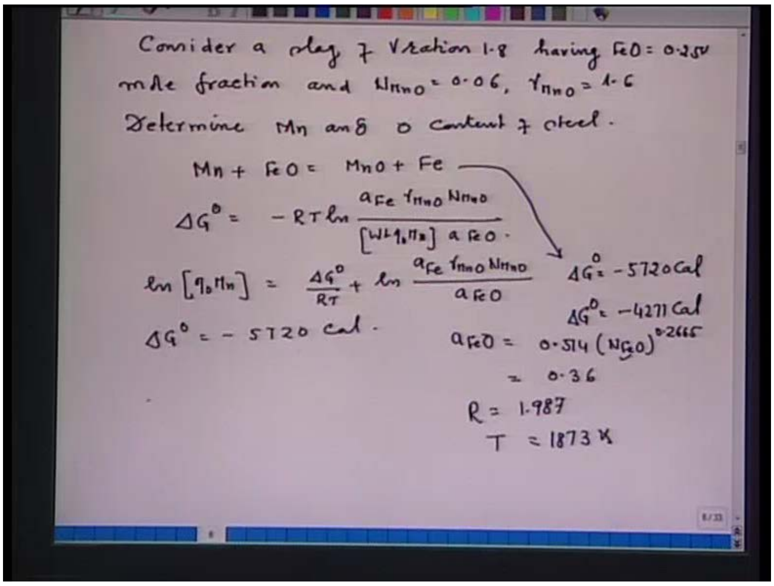

Consider a slag of V ratio 1.8 having FeO = 0.25 mole fraction and $N_{MnO} = 0.06$, $\gamma_{MnO} = 1.6$

Determine Mn and O content of steel.

$$Mn + FeO = MnO + Fe$$

$$\Delta G^0 = -RT\ln \frac{a_{Fe}\,\gamma_{MnO}\,N_{MnO}}{[wt\%Mn]\,a_{FeO}}$$

$$\ln[\%Mn] = \frac{\Delta G^0}{RT} + \ln \frac{a_{Fe}\,\gamma_{MnO}\,N_{MnO}}{a_{FeO}}$$

$\Delta G^0 = -5720$ cal.

$\Delta G^0 = -5720$ Cal

$\Delta G^0 = -4271$ Cal

$a_{FeO} = 0.514\,(N_{FeO})^{0.2665}$

$= 0.36$

$R = 1.987$

$T = 1873$ K

Let us consider a slag of V ratio. V ratio means basicity. Basicity means all basic oxide upon all FeO oxide equal to 1.8 having FeO that is equal to 0.25 mole fractions and mole fraction of MnO that is equal to 0.06. We will assume that gamma MnO is given to us that is equal to say 1.6.

Now, let us determine the manganese and O content of steel. We will use a reaction manganese plus FeO that is equal to MnO plus iron. We can write down delta G naught that is equal to minus RTln activity of iron gamma MnO N MnO weight percent Mn into activity of FeO or we can put it ln percent manganese that is equal to delta G naught upon RT plus ln activity of iron gamma MnO N MnO upon activity of FeO.

So, if you want to calculate the percentage manganese which is in equilibrium for a slag, which is having a V ratio 1.8 and mole section of FeO is 0.25, then we can use this expression for determining the manganese content at equilibrium.

For that, we need a delta G naught value. Now, delta G naught in one source, it is given minus 5720 calorie; this delta G naught is for this particular reaction. (Refer Slide Time: 47:08) Another source gives delta G naught that is equal to minus 4271 calorie and this source is our equation number 9, where I put the delta G naught is minus 123516 plus 56.41 T.

If you put T is equal to 1873 kelvin then we get the value of delta G naught minus 4271 calorie.

So, these are the two sources. I just want to illustrate that ultimately, the calculation of manganese will depend upon from which source, the value of free energy change has been taken because there is no problem in the equation; only the value which you substitute, accordingly you may get the different values of percentage manganese in equilibrium. So, that is why I thought I will take two sources from here.

Say for example, if I take delta G naught that is equal to minus 5720 calorie. Then what I do? I put now into this expression. This expression also requires, I should know what the value of activity of FeO is.

Now, we recall activity of FeO can be determined from 0.514 N FeO raise to the power 0.2665. This equation I have already given. If you substitute the value of N FeO that is 0.25 over here, then we get activity of FeO that is equal to 0.36. So, we know now activity of FeO, we know gamma MnO, we know N MnO, activity of iron we take equal to 1, delta G naught is known to you and R we substitute 1.987 in the respective unit, T we take 1873 kelvin.

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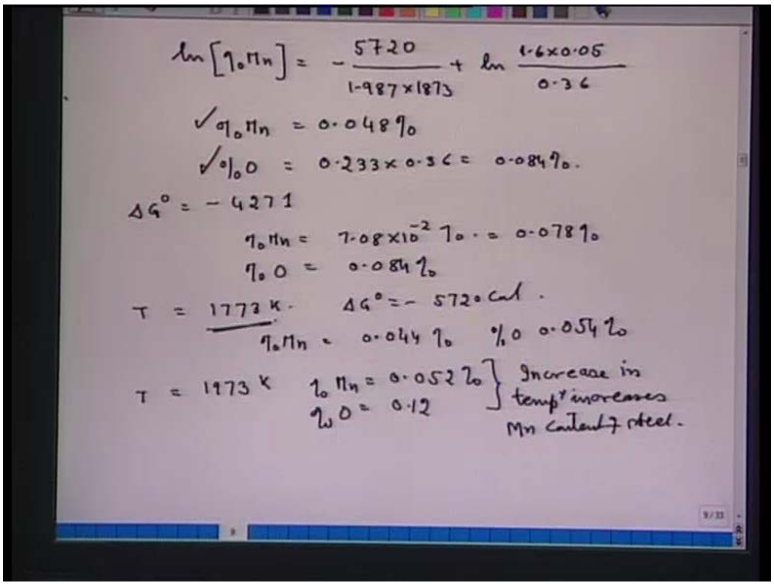

$$\ln[\%Mn] = -\frac{5720}{1.987 \times 1873} + \ln\frac{1.6 \times 0.05}{0.36}$$

✓ $\%Mn = 0.048\%$

✓ $\%O = 0.233 \times 0.36 = 0.084\%.$

$\Delta G^\circ = -4271$

$\%Mn = 7.08 \times 10^{-2}\% = 0.078\%$

$\%O = 0.084\%$

$T = \underline{1773\,K}$. $\Delta G^\circ = -5720$ cal.

$\%Mn = 0.044\%$ $\%O$ 0.054%

$T = 1973\,K$ $\left.\begin{array}{l}\%Mn = 0.052\% \\ \%O = 0.12\end{array}\right\}$ Increase in temp^r increases Mn content of steel.

Then we calculate, for example, say ln percent manganese that will be equal to minus 5720 upon 1.987 into 1873 plus ln 1.6 into 0.05 upon 0.36.

If we solve, then we will get percentage manganese that is equal to 0.048 percent in equilibrium under the condition and percentage oxygen at 1873, you recall, we determined for activity of FeO, the percentage oxygen at saturation was 0.233 at 1873 kelvin. We just multiply by the activity of FeO that we have determined now, which is equal to 0.36.

So, percentage oxygen is equal to 0.233 into 0.36 and that is equal to 0.084 percent. So, this calculation says that manganese can be very easily oxidized under the oxidizing condition.

Now, if I take another source say for example, in another source, delta G naught was equal to minus 4271 and if I calculate the value of percentage manganese and percentage oxygen, the method is similar, all that for delta G naught earlier I substituted 5720, now I will be substituting 4271.

So, if I do that calculation, I will be getting percentage manganese that is equal to 7.08 into 10 to the power minus 2 percent and percentage O that is equal to 0.084 percent; percentage O will not change because activity of FeO is the same. So, percentage manganese, I can also write down as 0.078 weight percent.

All that it says that manganese can be oxidized very easily under steel making condition. The sources are different; therefore, you are getting the different values of manganese, but, it does not matter at all because all that will depend upon which source you have used to calculate the value of manganese and what values you have substituted. I have substituted the value of gamma MnO is say 1.6. You may get a different source which may have different value. I calculated the value of activity of FeO is 0.36, from other source you may get 0.4 or 0.5 because there are several sources available, but it does not matter; all that it says that manganese can be oxidized very easily.

Now for example, if I want to illustrate that the low temperature favours your oxidation of manganese, what I do now? I take T is equal to for example, 1773 kelvin and I use delta G naught value is minus 5720 calorie.

Then I will be calculating percentage manganese that will come equal to 0.044. So, percent manganese was equal to 0.044 percent and percent oxygen that is in equilibrium with this temperature is equal to 0.054 percent.

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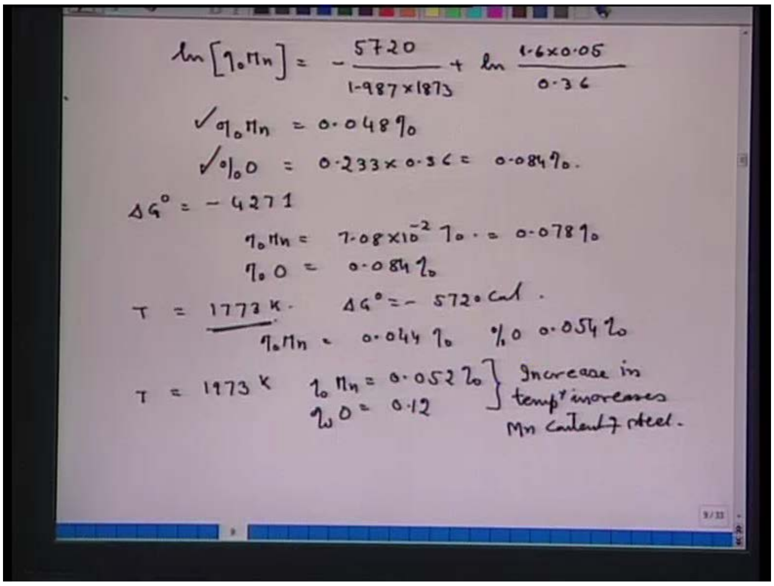

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Now, this value is to be compared with 0.048 percent earlier for 1873. Now, we are getting 0.044 percent; that means, decreasing temperature favours oxidation of manganese.

Similarly, if we take for example, T is equal to 1973 kelvin then we can calculate percent manganese that is equal to 0.052 percent and percent O that is equal to 0.12 percent.

Naturally, the percent oxygen will also be affected because of the temperature; as temperature increases, the solubility of oxygen also increases.

So, we are getting percent O is 0.12 percent at 1973 kelvin. What it says from here is that increase in temperature increases Mn content of a steel whereas, for 1773, our conclusion decrease in temperature will increase the oxidation of manganese.

That means, decrease in temperature favours the oxidation of manganese and increase in temperature favours the reduction of manganese. That is what I have shown by taking the calculation at different temperatures.

So, remember the oxidation of manganese and reduction of manganese. They are the most important reaction in steel making. We will use it, when I will do the practice. Now, in the next lecture, we are going to take the other reactions for example, silicon, carbon and phosphorous and that is all.