Reduction of Iron Oxide by Carbon in Stainless Steelmaking Slags

M. Divakar*, M. Görnerup**¹ and A. K. Lahiri

**Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL 35487-0202, USA*

***Uddeholm Technology AB, Urvåv. 2, S-68340, Uddeholm, Sweden.*

Department of Metallurgy, Indian Institute of Science, Bangalore - 560 012, India.

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ABSTRACT

Kinetics of iron oxide reduction by carbon in typical stainless steelmaking slags where slag chemistry changed continuously due to dissolution of Al_2O_3 was studied. The progress of reaction was monitored by X-ray equipment. A foamy slag formed in all cases. The foaming characteristics and the rate of reduction were dependent on the slag composition. Both chromium and vanadium oxides reduce the reaction rate. Change of slag chemistry due to dissolution of Al_2O_3 does not affect the reaction rate. The rate controlling step depends on the stirring of slag due to gas generation by simultaneous reduction of oxides.

Key Words: FeO reduction, simultaneous reduction, foam formation, slag.

1. INTRODUCTION

The reduction of iron oxide from slag by carbon has been studied by a number of investigators /1-16/. These studies confirm that the reduction by carbon takes place by gaseous intermediates according to the following reactions:

The rate limiting step for reduction varies with the amount of FeO in the slag. In high FeO content systems, all three types of rate controlling steps, diffusion /12/, chemical reaction /11,13/ and mixed control /14/ have been found to be rate limiting. At lower FeO levels mass transport of FeO is reported to be the rate limiting step /11/. The reaction rate depends on the type of carbon as well. Carbon dissolved in metal reduces FeO in slag at a faster rate than solid carbon although the reaction mechanism remains same /9,10/. All these studies except those by Görnerup /15,16/ were on the reduction of only FeO from slag. Görnerup studied simultaneous reduction of iron and chromium oxides from the EAF slag and found that the reduction mechanism is not affected by simultaneous reactions.

During EAF stainless steelmaking iron oxide, chromium oxide and sometimes vanadium oxide are simultaneously reduced. Furthermore, during the progress of reaction, the slag chemistry changes due to dissolution of fluxes and lining. To understand the effect of interaction of various phenomena on the reduction of iron oxide, the present study was made where reduction of iron, chromium and vanadium

At the time of work Dr. Divakar was at the Department of Metallurgy, Indian Institute of Science, Bangalore, India and Dr. Görnerup was at Royal Institute of Technology, S-10044, Stockholm, Sweden.

Fig. 1: Schematic diagram of the experimental setup

oxides take place along with dissolution of Al_2O_3 in the slag.

2. EXPERIMENTAL TECHNIQUE

The experimental equipment and procedure used in this study are similar to those presented in our earlier work [17]. Figure 1 shows the schematic diagram of the experimental setup. The graphite crucible was lined with an alumina tube of outer diameter 45mm and thickness 2.5mm. 50g of premelted slag was used in these experiments. Table 1 lists the slag compositions that were studied. Experiments were conducted in the temperature range 1550-1650°C. X-ray equipment along with a video recording facility was used to monitor the

reduction process. In each of the experiments, the slag samples of about 0.8-1.0 g collected at different time intervals were analyzed. The respective amounts of oxides were determined assuming that weight of CaO in the slag remained unchanged. All slag samples were analyzed in the sequenced differentiated x-ray spectrometer, Siemens SRS-303. The maximum relative error when using this equipment is $\pm 2\%$.

3. RESULTS AND DISCUSSION

The video recording was viewed to follow the various phenomena that occurred during the reaction. The recording showed foam and emulsion formation, variation in foam height and the gas bubble size during

Table 1
Slag Compositions Studied
Basicity = $\text{wt}\%\text{CaO} / \text{wt}\%\text{SiO}_2$

Basicity	wt% Al_2O_3	wt% FeO	wt% MgO	wt% Cr_2O_3	wt% MnO	wt% V_2O_5
1, 1.5	7	6	0, 5, 10, 15	2, 5, 10, 14	2	0, 2, 5

the reduction process. Figure 2 shows an x-ray image where the slag was lifted at certain places during the reduction process. This indicates that the gas generation did not take place uniformly at the bottom of the crucible. Figure 3 shows another x-ray image of the reduction process where gas generation is observed at the bottom and splashing is seen at the top of the slag melt. Figures 2 and 3 are typical x-ray pictures grabbed

Fig. 2: X-ray image showing the lifting of the slag during the reduction of slag in a graphite crucible

Fig. 3: X-ray image showing (a) gas generation and (b) splashing during the progress of the reaction

from the video recording during the reduction process. It can be seen that the reduction behavior was different for different slags. The reduction of FeO takes place both at the metal/slag and graphite/slag interfaces. But, in this study the two processes could not be clearly distinguished. Some of the pictures clearly showed the presence of metal droplets at the bottom. So, the reaction interface was not confined to the crucible bottom.

During the reduction process, gas generation led to the formation of foam whose height changed with the progress of reaction. The height of foam was measured manually from the video recording at different time intervals. The gas generation rate and the foam height had no direct relationship.

Figures 4a and 4b show the variation of weights of the oxides with time in one of the slag compositions studied at 1873 K. Figure 4a shows a steep rise in Al_2O_3 content of the slag followed by a saturation stage. CaO and SiO_2 remain unchanged in their respective weights throughout the reaction period. Figure 4b shows the variation of other oxides that are grouped in the lower portion of the Fig. 4a. MnO and MgO are not reduced while FeO, Cr_2O_3 and V_2O_5 are reduced. In the present experiments, the slag composition was changing continuously mainly due to the dissolution of Al_2O_3 . As a first approximation, the rate of FeO reduction can be represented as,

$$-\frac{dW_{\text{FeO}}}{dt} = \alpha (\% \text{FeO} - \% \text{FeO}^{eq}) \quad (1)$$

where α is the apparent rate constant, $\% \text{FeO}$ is the amount present at any time t and $\% \text{FeO}^{eq}$ is that in equilibrium with graphite. Equation (1) is usually written in the following manner,

$$-\frac{W_o}{dt} \frac{d\% \text{FeO}}{dt} = \alpha (\% \text{FeO} - \% \text{FeO}^{eq}) \quad (2)$$

where W_o is the total weight of the slag. Since the total weight of the slag was changing in the present case, Eqn. (2) could not be used for integration. The term $\% \text{FeO}^{eq}$ is very low and is neglected. Integrating Eqn. (1) from $t = 0$ to $t = t$, we have,

$$W_{FeO}^o - W_{FeO} = \alpha \int_0^t \%FeO \cdot dt \quad (3)$$

where W_{FeO}^o and W_{FeO} are the initial weight and weight at any time t of FeO. The right hand side of Eqn. (3) was evaluated numerically using the trapezoidal rule. The apparent rate constant can be determined by

Fig. 4: The variation of slag composition during the progress of reduction for a slag containing 7% Al₂O₃, 5% MgO, 6% FeO, 5% Cr₂O₃, 2% MnO and 2% V₂O₅ at 1873 K

plotting the left-hand side term against the numerically evaluated integral. Figure 5 shows a typical plot of FeO reduction for different slags at 1823 K. The reduction rates vary widely with slag compositions. All the curves are almost straight lines and the apparent rate constant was obtained by means of linear regression. This procedure is carried out at all the temperatures for a given slag composition. The rate constant α is directly proportional to surface area of reaction. Almost linear plots in Fig. 5 suggest that during the progress of reaction there was no significant change in the surface area of reaction. Since, except at the initial stage, reaction takes place both by carbon dissolved in metal and graphite, above observation suggests that on the whole, the total contact area of slag/metal-droplets and slag/graphite was constant. It is interesting to note that, although there was a sharp dissolution of Al₂O₃ into the slag, the rate of FeO reduction was not affected.

Fig. 5: Typical reduction of FeO in slags containing different amounts of Cr₂O₃ and V₂O₅ at 1823 K

3.1. Effect of Basicity

Figure 6 shows the effect of basicity (wt% CaO/wt% SiO₂) of the slag on the reduction rate of FeO. The rate constants for slags having basicity 1.0 were found to be slightly higher than those having basicity 1.5. However, the effect of basicity of the slag on the reduction of FeO is not very significant. The effect of slag basicity on the rate of Cr₂O₃ reduction showed a similar behavior [17].

Contrary to the present observation Paramguru /9,10/ and Görnerup /16/ reported that the rate of FeO reduction increases with increasing basicity up to a value of 1.5 and then decreases sharply. This anomaly can be attributed to the dissolution of Al_2O_3 or slag chemistry.

Fig. 6: The effect of basicity on the rate of FeO reduction with temperature. The slags contained 7% Al_2O_3 , 5% MgO , 6% FeO , 10% Cr_2O_3 and 2% MnO

3.2. Effect of Cr_2O_3 Content

Figure 7 shows the change in the rate constant (α) with initial wt% Cr_2O_3 for different slags at three temperatures. The figure shows that for each type of slag, the reaction rate decreases with increase of % Cr_2O_3 at all temperatures. All the slag compositions contained FeO content in the range 5.5-5.9 wt%. The decreased reduction rates at higher Cr_2O_3 contents of the slag can be attributed to association of the oxides in the form of spinel.

3.3. Effect of MgO Content

Figure 8 shows the effect of MgO content of the slag on the reduction rate at all the three temperatures. The rate falls sharply from 0% MgO to 5% MgO at all temperatures. The reduction of Cr_2O_3 showed a similar

Fig. 7: The effect of initial Cr_2O_3 content in the slag on the reduction rate of FeO at different temperatures

Fig. 8: The effect of MgO content in the slag on the reduction rate of FeO at different temperatures

behavior with MgO content of the slag as shown in Fig. 9 /17/. In the slag containing 5% MgO liquid iron droplets were present at the bottom of the crucible and their size reduced with the progress of the reaction. However, in the slag containing very low MgO content, small droplets were found to be suspended in the foam. This suggests that the surface area for reduction was much larger in this slag than in the former. So the higher

Fig. 9: The effect of MgO content in the slag on the reduction rate of Cr_2O_3 at different temperatures

reduction rates in Figs. 8 and 9 for slag containing very low MgO content may be attributed to the increase in the available surface area for reduction. Further increase in the MgO content of the slag did not show any definite trend in the FeO reduction behavior.

3.4. Effect of V_2O_5 Content

The rate of FeO reduction decreased with increasing V_2O_5 content of the slag. Figure 10 shows the effect of

Fig. 10: The effect of V_2O_5 content in the slag on the reduction rate of FeO at different temperatures

V_2O_5 on the reduction rate of FeO at two temperatures. The rate constant decreased sharply from 0 to 2% V_2O_5 at both the temperatures. Further increase in the amount of V_2O_5 decreases the rate but not very sharply. The effect of V_2O_5 on the reduction rate of Cr_2O_3 from the same slag was similar [17]. It is known [18] that the presence of V_2O_5 , a surface-active oxide in slags, strongly promotes the formation of foam. The variation of average foam height with increasing V_2O_5 content of the slag is shown in Fig. 11 at two temperatures. The average foam height increased with increasing V_2O_5 content of the slag. A small addition of V_2O_5 to the slag leads to severe foaming thereby reducing the amount of liquid slag in contact with the reductant. This resulted in sharp decrease in the reduction rate of FeO (Fig. 10) from 0 to 2% V_2O_5 . Since the compound $\text{FeO} \cdot \text{V}_2\text{O}_5$ is stable at high temperature, the decrease of reaction rate is partly due to association of FeO with V_2O_5 .

Fig. 11: The effect of V_2O_5 content on the average foam height in the slag during the reduction process at two temperatures

3.5. Activation Energy

Figure 12 represents the $\ln(\alpha)$ vs. $1/T$ plot of FeO reduction for slags containing different Cr_2O_3 levels. The activation energies in slags containing initial wt% Cr_2O_3 of 2, 5, 10 and 14 were 83, 24, 228 and 164 kJ/mol respectively. Activation energy of 87 kJ/mol in a slag containing 5% Cr_2O_3 was reported in a previous

Fig. 12: The plot of $\ln(\alpha)$ versus $1/T$ of FeO reduction for slags containing different Cr_2O_3 levels

work/16/. Table 2 shows the literature data on the activation energy for FeO reduction, which varies between 88 and 314 kJ/mol. The present study shows that, depending on the slag composition, the activation energy lies in the range 24-579 kJ/mol.

The reported values /19-21/ for the diffusion of iron oxide in slags vary from 73 to 167 kJ/mol. The mechanism for FeO reduction in slags having the

activation energy values in the range 70-170 kJ/mol is the diffusion of iron oxide in the slag phase. In slags having activation energies about 40 kJ/mol the mechanism of FeO reduction is the diffusion of carbon in the Fe-C alloy phase since the reported value /19/ for carbon diffusion in Fe-C alloys is 42 kJ/mol. Values higher than 170 kJ/mol indicate chemical reaction or mixed controlled. Very high values of activation energy, 482 and 579 kJ/mol, obtained for V_2O_5 containing slags suggest strong association between iron and vanadium oxides in the slag.

Figure 13 shows the variation of activation energy of FeO reduction with average gas generation rate due to reduction at 1823 K. The graph shows that the activation energy for FeO reduction decreases with increase in gas generation rate. The mixing of the slag melt during the progress of the reaction depends on the rate of gas evolution. If the mixing is intense, the length of diffusion path in the slag is low and the rate controlling step becomes diffusion of carbon in the metal phase. If the stirring intensity is less, then the reduction becomes slag phase diffusion controlled. Gas generation rate, in the present case, depends on the rates of reduction of FeO, Cr_2O_3 , and V_2O_5 . So the presence of other reducible oxides affects the reduction rate of FeO both by association and by affecting the gas generation rate.

Table 2
Literature Data on the Activation Energies for FeO Reduction

Activation Energy, kJ/mol	Temperature, °C	System	Reductant	Researcher(s)
-	-	FeO in 'slag' (unknown composition)	C + C in Fe	Kim et al /7/
314	-	-	C _{steel crucible}	-
130	1420-1620	FeO (l)	C _{alumina crucible}	Sato et al /6/
184	-	-	C in Fe	-
90	1200-1400	CaO-SiO ₂	C	Paramguru et al /9/
87.9	1200-1400	CaO-SiO ₂	C in Fe	Paramguru et al /10/
223	-	CaO-SiO ₂ -MgO	C	Zhou /8/
135	1320-1600	CaO-MgO-SiO ₂ -FeO-FeO _{1.5}	CO (g)	Graenzdoerffer et al /11/

Fig. 13: The effect of average gas generation rate at 1823 K on the activation energy for FeO reduction for various slags. The base slag composition is 7% Al_2O_3 , 6% FeO, 5% MgO, 10% Cr_2O_3 and 2% MnO, Basicity = 1.5

○: base slag with varying Cr_2O_3 content; □: base slag with varying V_2O_5 content; △: base slag with varying wt% MgO; +: Basicity = 1.0

4. EFFECT OF CONTACT AREA

The rates of heterogeneous reactions depend on the contact area between the reactants. In the present experiments several phenomena such as foaming, gas generation and lifting of the slag took place. The foam height varied with the slag composition and progress of reaction for any given slag. In some cases liquid iron droplets were suspended in the foam. Therefore, the contact area for both metal/slag and graphite/slag interfaces varied with the experimental conditions. It has already been mentioned that the lower rate of reduction of slag containing 5% MgO compared to that of 0% MgO is due to lower surface area for reduction. Very low activation energy value (24 kJ/mol) for FeO reduction in the slag containing 5% Cr_2O_3 appears to be due to decrease in the surface area for reduction at higher temperatures. The activation energy for reduction of Cr_2O_3 in this slag was also very low [17] supporting the above view.

The activation energies were calculated with the

assumption that the surface area for reaction is independent of temperature. The variation of activation energy with average gas generation rate shown in Fig. 13 and the values of activation energy indicate that the assumption is valid except for the slag containing 5% Cr_2O_3 .

5. CONCLUSIONS

The surface area of reaction and rate of FeO reduction depend on the slag chemistry. The reduction rate decreases with increase in % Cr_2O_3 and % V_2O_5 of slag. The reduction rate is not affected by the simultaneous dissolution of Al_2O_3 .

The activation energies for the reduction of FeO range from 31 to 579 kJ/mol. The mechanism for the reduction of iron oxide depends on the intensity of stirring due to gas generation by simultaneous reduction reactions. At high gas generation rate the reduction is controlled by carbon diffusion in iron. The strong association between iron and vanadium oxides results in very high activation energies of 482 and 579 kJ/mole in V_2O_5 containing slags. The change in the surface area of reaction with temperature can lead to very low values of activation energy.

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