Interfacial Reactions of Low Iron-containing Slag with CO_2-CO Mixtures

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ABSTRACT

Kinetics of redox reaction between CO-CO_2 and CaO-MgO-SiO_2-10%FeO_x melts was studied at temperatures in the range of 1244 to 1500°C and under conditions where mass transfer in the gas phase or the liquid slag was not the rate limiting step. The measured rates of reduction and oxidation of slags by CO_2-CO showed strong dependence on the oxidation state of the slag as well as on the CO_2/CO ratio and temperature. The rate data are consistent with the expected behavior for the interfacial rate of formation/dissociation of CO_2 as the rate controlling step. The measured apparent first order rate constant for reduction was found to be nearly proportional to the Fe^{3+}/Fe^{2+} ratio in the low iron oxide containing slags. This is consistent with a reaction mechanism which involves single charge transfer between the Fe^{3+}/Fe^{2+} and adsorbed CO_2 species at the interface. The deduced activation energy for the reaction is about 147 kJ/mol.

Key words: interfacial kinetics, redox reaction, bath smelting slags, oxygen transfer/evolution.

1. INTRODUCTION

The recovery of metals from slags is an essential stage in many pyrometallurgical processes. In reactions between metallurgical melts and reactants such as carbonaceous materials, gaseous species (eg. CO_2 and CO) play important roles in determining the process route and the resulting product. For high iron slags, insight into the gas-slag reactions has been gained especially through the work of Belton and his co-workers [1-6]. The rate phenomena involved in interfacial reactions between CO_2-CO and iron oxide-rich slags have been investigated and the reaction mechanism is now reasonably well understood. However, very little information is known about the rates and mechanisms of the interfacial chemical steps for slags of low iron oxide content and in particular, those relevant to the proposed iron bath smelting processes, ie. slag containing less than 10 wt% FeO. Specifically, kinetic data on the rate of the oxygen transfer between slag and gas, through reduction or oxidation, would be highly desirable for improving our understanding of the kinetic behavior of molten slags. Moreover, it would also open the way to a more complete knowledge of the effect of iron and other transition metals on the kinetics of interfacial reactions between slags and gases. In this paper, some results of a study on the interfacial rate of redox reaction between slags and gases are presented. In particular, the reduction and oxidation and oxygen evolution by reaction with CO_2-CO gas mixtures of a low iron-containing CaO-MgO-SiO_2 based slag were investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Iron free master slag with basicity of about 0.7 (Basicity = (%CaO+%MgO)/%SiO_2)) was prepared by melting appropriate amounts of $CaCO_3$, MgO and SiO_2 (purity > 99%) in a Pt crucible. The homogenized master slag was then pulverized and doped with about 10 wt% of Fe_2O_3 before being remelted, quenched and pulverized for use in the equilibrium and kinetic experiments. The composition of the master slag in weight percent was : 28.9% CaO, 54.5% SiO_2 , 7.2% MgO, 9.4% Fe_2O_3.

Ar and CO_2 gases were purified by passing through columns of silica gel and anhydrous magnesia perchlorate to remove moisture. The gases were then passed through copper turnings kept at about 500 °C to remove traces of oxygen. CO and Ar were also passed through ascarite columns to remove CO_2. The CO_2 and CO were then mixed in appropriate ratios using pre-calibrated mass flow-controllers, and passed through a glass beads column before being delivered to the furnace through a gas inlet tube.

2.2 Procedure

A $MoSi_2$ tube furnace was used for carrying out the experiments on the redox reactions. The work tube of the furnace was fitted with water cooled brass end caps and the atmosphere inside the furnace was isolated by a brass flange at the top and a polyethylene film at the bottom. The temperature inside the furnace was measured by a type B (Pt-6%Rh / Pt-30% Rh) thermocouple placed near the crucible containing the melt in the hot zone of the furnace.

In each experiment, about 0.2 g of slag was placed inside a Pt crucible (10 mm ID x 12 mm deep) and melted at the required temperature under a controlled atmosphere. The crucible was suspended by a platinum wire which passed through a gas inlet tube (8 mm OD and 5 mm ID) held vertically within the alumina reaction tube. The crucible was so placed that the surface of the melt held in it was about 6 mm below the tip of the gas delivery tube. The melt was pre-equilibrated with air or mixtures with desired CO_2/CO ratio and then reacted with a more reducing or oxidizing gas mixtures with CO_2 -CO ratio of 5, 10, 25 and 40. After a specified time of reaction, the crucible was quickly quenched in water. Time zero was determined by assuming plug flow for the gas with the flowrate of 600 cm^3/min to sweep the volume (about 10 ml) from the switching valve to the reaction zone. The quenched crucible containing a thin film of slag was then dried and used for determination of total and ferrous iron content by the conventional titration technique[7].

3. RESULTS AND DISCUSSION

Examples of the kinetic curves are shown in Figure 1. These were obtained by pre-equilibrating the slag in air and subsequently reducing by CO_2-CO mixtures at 1345°C. Slopes of these curves were used to derive rate and rate constant for further analysis.

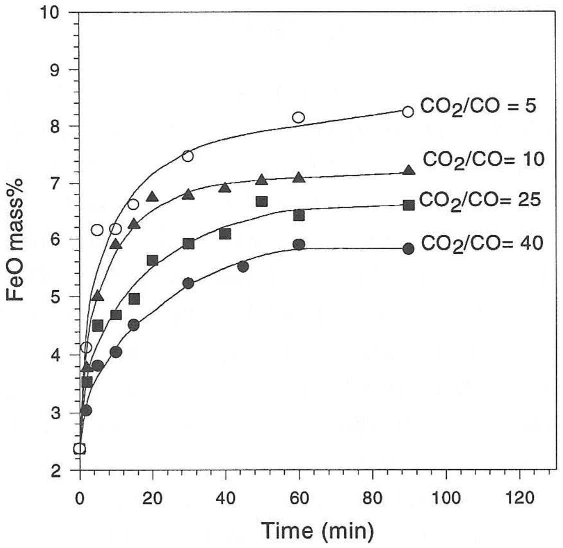

Fig. 1. Variation of slag composition with time in the reduction of slag with 10 wt% FeO_x by CO_2/CO gas mixtures at 1345°C. Sample was pre-equilibrated in air and reduced in CO_2/CO ratio of 5, 10, 25, 40.

3.1 Rate limiting steps

The aim of this study was to investigate the rate of interfacial reaction. It is critical to overcome rate limitations by processes like the diffusion in the melt and the mass transfer in the gas phase.

Compared to the reaction with iron-rich slags, the reaction with low iron slag was generally much slower. Results obtained in terms of the rate at varying flowrates are shown in Figure 2. The open circle and closed triangle symbols show the result for calcium ferrite with 80 wt% of FeO_x from Sun et al.[5] and Tran et al. [8], respectively, at 1300 °C. Sun et al.[5] have used a similar experimental set up and obtained their rates from isotope exchange measurements. Samples from both studies were pre-equilibrated in CO_2/CO mixtures of 10 and reduced in CO_2/CO mixtures of 5. At low gas flow rate (below 300 cm^3/min), there is some dependence of the reduction rate on the gas flow rate. However, at higher gas flow rate, the reduction rates seem to be independent of gas flow rate. This suggests that above 500 cm^3/min, mass transfer in the gas phase was sufficiently fast and not a rate controlling step. For a low iron containing slag ($CaO-MgO-SiO_2$-10wt% FeO_x), with the rate even lower than the rate for calcium ferrite, mass transfer in the gas phase should not be the rate controlling step with gas flowrate in the vicinity of 600 cm^3/min.

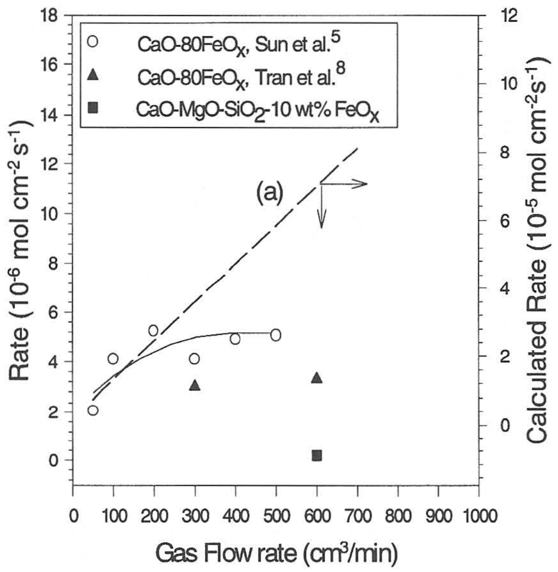

Fig. 2. Demonstration of the independence of the rate on the reaction gas flowrate for CaO-80%FeO_x and $CaO-MgO-SiO_2$-10%FeO_x. Line (a) denote the rate of mass transfer in the gas phase calculated with the correlation of Saito et al[9].

Furthermore, comparison of the measured rate with the rate of mass transfer calculated using the relevant correlation[9] supported the conclusion that the gas phase mass transfer was unlikely to be the rate limiting step, when CO_2-CO gas mixtures at the selected flowrate were used to measure reduction and oxidation rate of the low iron slags.

To test whether the rate was controlled by interfacial chemical reaction or by diffusion for the low iron-containing slag system, a series of experiments was carried out in which the ratio of CO_2/CO was kept constant, thereby maintaining the oxidizing potential of the gas mixture, but the mixture was subjected to varying degrees of dilution with argon. If the reaction kinetics were controlled by diffusion in the slag phases, then the rate should be independent of dilution by argon. However, if the rate-controlling mechanism was interfacial chemical reaction, dilution of the mixture with argon was expected to reduce the reaction rate.

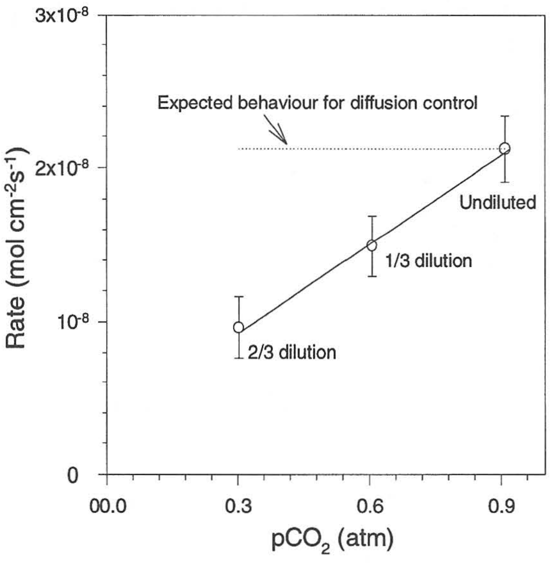

Fig. 3. The first order dependence of the average initial rate with p_{CO2} diluted with argon in the reaction gas with $p_{CO2}/p_{CO} = 10$ at 1345°C for $CaO-MgO-SiO_2$-10%FeO_x slag.

Figure 3 shows the measured rate of oxidation versus p_{CO2} with varying degrees of dilution by argon. The slag was first pre-equilibrated with $CO_2/CO = 5$ then oxidized with $CO_2/CO = 10$. It was observed that the rate of oxidation of iron in the melt decreases as the reacting gas mixture is diluted. The results were consistent with the rate of CO_2 dissociation being first order with respect to the partial pressure of CO_2 in the reaction gas[5] :

$$v = k_a p_{CO2} (1 - a_o\ p_{CO}/ p_{CO2}) \qquad [1]$$

where; k_a is the apparent first order rate constant for the dissociation of CO_2 on the surface of the melt or the oxidation of the slag by CO_2, a_o is the oxygen activity in the melt with the standard state defined at $p_{CO2} / p_{CO} = 1$. In other words, the reaction rate determined using the current procedure was most likely controlled by the interfacial chemical reaction.

3.2 Rate of reduction in CO_2-CO mixtures

Figures 1 and 4 show the results of reduction of CaO-MgO-SiO_2-FeO_x slag which were initially equilibrated in air and in various CO_2 /CO gas mixtures.

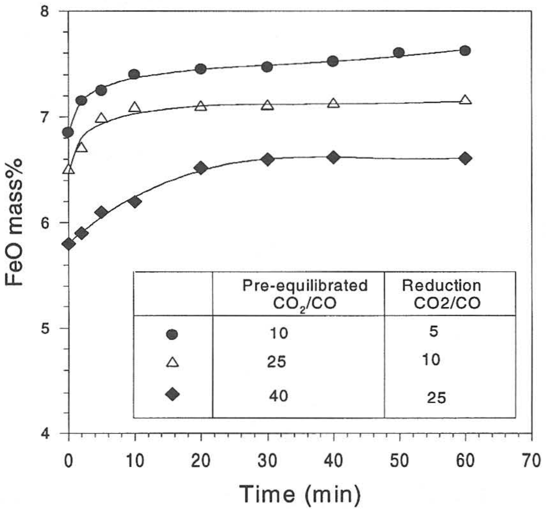

Fig. 4. Variation of slag composition with time in the reduction of slag with 10 wt% FeO_x by CO_2/CO gas mixtures at 1345°C. Samples were pre-equilibrated in CO_2/CO mixtures of 10, 25 and 40 and reduced in CO_2/CO mixtures of 5, 10 and 25, respectively.

Data plotted in these figures were analysed to obtain the rate of reduction by CO_2-CO. The overall reduction reaction being considered in this investigation was:

$$(Fe_2 O_3) + CO (g) = 2(FeO) + CO_2 (g) \qquad [2]$$

The rate of the reaction, v, in mol cm^{-2} s^{-1}, was given by:

$$v = \frac{W}{14{,}400A} \frac{d\,pct\,FeO}{dt} \qquad [3]$$

where; W is the mass of the melt (g) and A is the reaction surface area(cm^2).

The initial stage of reduction was approximated by linear variations with reaction time. The slopes of initial straight lines were used to calculate the reaction rate. These values are listed in Table I. The initial reaction rate showed a decreasing trend for the series of runs from the top to the bottom.

Table I: The average initial rate of reduction of the slag pre-equilibrated in air and reduced by CO_2/CO mixture.

Pre-equilibrate conditions	Reducing CO_2/CO	v x 10^7 mol cm^{-2} s^{-1}	Mid Fe^{3+}/Fe^{2+}	k_a'x 10^6 mol cm^{-2} s^{-1} atm^{-1}
air	5	2.23	1.137	1.37
air	10	1.55	1.276	1.76
air	25	1.26	1.407	3.51
air	40	0.84	1.95	3.65
10	5	0.21	0.22	0.301
25	10	0.13	0.32	0.323
40	25	0.091	0.44	0.796
40	10	0.24	0.3	0.682

Also listed in Table I are rate constants calculated according to the rate law[1]:

$$v = k_a' \ (p_{CO} - p_{CO2} / a_o) \qquad [4]$$

where, k_a' is the apparent first order rate constant for the formation of CO_2 on the surface of the melt or the reduction of that slag by CO, a_o is the oxygen activity in the melt with the standard state defined as $pCO_2/pCO = 1$.

For calculation of a_o and hence k_a', the equilibrium relationship[10] :

$$\log (Fe^{3+}/Fe^{2+}) = 0.494 \log(pCO_2/pCO) - 1.117 \quad [5]$$

deduced from equilibrium studies (as shown in Figure 5) was used.

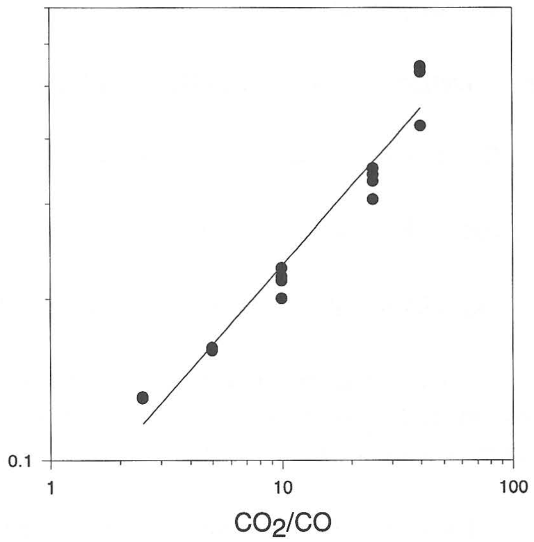

Fig. 5. The equilibrium Fe^{3+}/Fe^{2+} ratio for a $CaO-MgO-SiO_2-10FeO_x$ slag as a function of CO_2/CO ratio at 1345 °C[10].

By assuming that the initial rate refers to the average melt composition at about the midpoint of the linear range, the values of the apparent first order rate constant were obtained and these values are listed in the last column of Table I.

It can be seen that the values of k_a' increase with increasing a_o and Fe^{3+}/Fe^{2+} ratio. These results are plotted in Figure 6 as triangles. The line going through these points is given by the regression equation:

$$k_a' = 1.02 \times 10^{-7} a_o^{0.53 \pm 0.07} \quad [6]$$

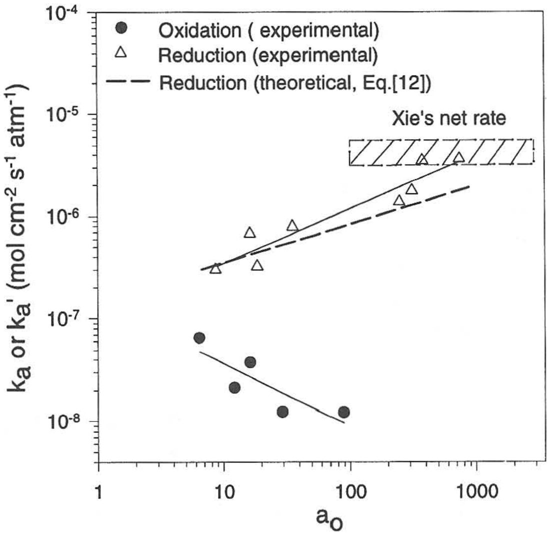

Fig. 6. Dependence of the first order rate constant for reduction and oxidation reaction on the activity of oxygen of the slag at 1345°C.

3.3 Oxygen evolution and oxidation reaction rate

The redox reaction of molten slags with CO_2-CO gas is basically a process of oxygen transfer between the melt and the gas. Xie[11] has suggested that when an oxidized slag containing iron oxide is exposed to a flowing neutral gas (such as argon), the dissociation of Fe_2O_3 by the reaction:

$$(Fe_2O_3) = 2\,(FeO) + 1/2\,O_2\,(g) \quad [7]$$

may occur with the release of oxygen from slags.

Therefore, for reaction between melts and CO_2-CO:

Total reduction rate = rate of reduction by CO
+ rate of oxygen evolution [8]

In this study, the rates of oxygen evolution from the slag containing 10 % FeO_x into Ar or CO_2 flowing at about 600 cm^3/min were measured at 1345°C. The changes in slag composition are presented in Figure 7.

The rates were calculated from the initial slopes and the results are presented in Table II.

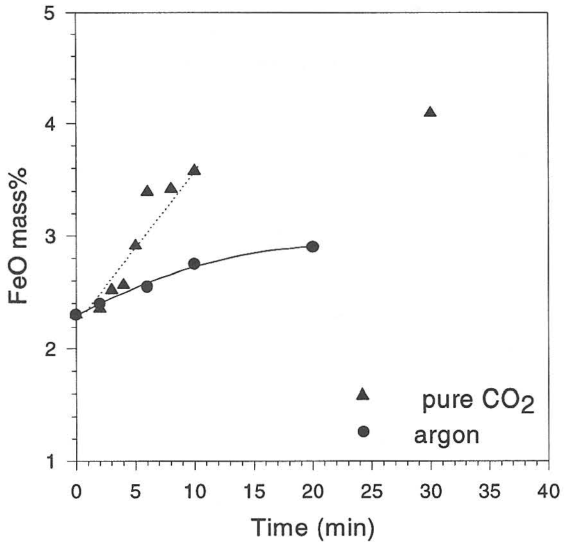

Fig. 7. Changes in FeO concentrations in flowing Ar and pure CO_2 as a function of time.

Table II: Rate of oxygen evolution

Pre-equilibrate conditions	Gas	v x 10^8 mol cm^{-2} s^{-1}
air	Ar	0.94
air	pure CO_2	3.60

The rate in CO_2 was about 3.6 x 10^{-8} mol cm^{-2} s^{-1}. Assuming this rate of evolution was independent of the CO_2/CO ratio of the imposed reaction gas, it could account for 15 to 45 pct of the total rate of reduction in CO_2-CO for slags initially equilibrated in air. However, accurate correction for the evolution is difficult because it is not known whether the reactions of oxygen evolution and the reduction by CO are completely independent and therefore additive in mixtures of CO and CO_2. The results have also shown that the rate of oxygen evolution under CO_2 as calculated from the rate of FeO formation was about 4 times the rate under Ar. Understandably, CO_2 can dissociate to give a small fraction of CO (about 3 x 10^{-3} atm) at temperature inside the furnace. Whether this was the cause of the difference in the rate of evolution is still to be clarified. CO_2 may also dissolve in the slag as carbonate. Judged from the data for CO_2 dissolution in CaO-FeO_x and CaO-Al_2O_3 slags [12-13], the solubility of CO_2 in the slag used in this study was not expected to be significant enough to change the bulk property of the slag. Therefore, the higher rate of oxygen evolution in CO_2 could not be accounted for by these simple factors.

To eliminate the uncertainty in the rate of reduction, due to the evolution of oxygen, a series of oxidation experiments was carried out so that the rate of reduction could be calculated based on the reversibility principle.

The oxidation is the reverse of Reaction [2] ie.,

$$2(FeO) + CO_2(g) = (Fe_2O_3) + CO(g) \quad [9]$$

The rate of this reaction is given by:

$$v = k_a (pCO_2 - pCO\ a_o) \quad (mol\ cm^{-2}\ s^{-1}) \quad [10]$$

where; k_a is the apparent first order oxidation rate constant, and a_o is the oxygen activity in the melt with the standard state defined as $p_{CO_2}/p_{CO} = 1$.

The rate of oxidation for 28.9% CaO - 54.5% SiO_2 - 7.2% MgO slag containing about 10 wt% FeO_x was determined over a range of CO_2/CO ratios (5 to 40) and pure CO_2. The procedure to obtain the rates and rate constants for oxidation reactions was similar to that used for reduction and the results obtained are summarized in Table III. The results in terms of the apparent rate constant as a function of oxygen activity of the melt on a logarithmic scale are plotted in Figure 6.

A regression of the experimental results (Table III) for oxidation gave:

$$k_a = 1.53 \times 10^{-7}\ a_o^{-0.62 \pm 0.22} \quad [11]$$

Accordingly, within the large uncertainty of the slope, the rate of reduction was formulated using the reversibility principle and was expressed by:

$k_a' = 1.53 \times 10^{-7} a_o^{0.38 \pm 0.22}$ [12]

Table III: The rate of oxidation of slag 28.9% CaO - 54.5% SiO_2 - 7.2% MgO containing about 10 wt% Fe_2O_3 at 1345 °C in CO_2/CO mixture.

Pre-equi $\frac{CO_2}{CO}$	Oxidizing $\frac{CO_2}{CO}$	v x 10^8 mol $cm^{-2}s^{-1}$	Mid $\frac{Fe^{3+}}{Fe^{2+}}$	k_a x 10^8 molcm^{-2} s^{-1} atm^{-1}
5	10	2.12	0.19	6.52
10	25	1.05	0.26	2.13
10	40	2.16	0.3	3.74
25	40	0.32	0.4	1.23
40	pure CO_2	1.08	0.69	1.21

The derived values of k_a' (from Equation [12]) have been plotted as the dashed line in Figure 6. These k_a' values are generally lower than the experimental values (triangles) and particularly so at high value of a_o. The difference is consistent with the evolution of oxygen contributing towards the overall reduction of Fe_2O_3 in slags.

Also shown in Figure 6 is the rate constant for 1350°C evaluated from the study of the reduction of Fe_2O_3 to FeO by Xie[11] for slags containing 47%CaO-40%SiO_2-13%Al_2O_3 and 5.8 wt% total Fe with the oxygen activity in the range from 100-3000. There appears to be good agreement at high oxidation states between the values of the rate constant from both studies according to the rate law expressed by Equation [4].

From the equilibrium study by the present authors[2], the dependence of Fe^{3+}/Fe^{2+} ratio on the oxygen activity in the melt could be expressed approximately by:

$(Fe^{3+}/Fe^{2+})^{2.02} \propto a_o$ [13]

Thus by combining Equation [6] and [13], the apparent rate constant for reduction could be written as:

$k_a' = k' \ (Fe^{3+}/Fe^{2+})^{1.06 \pm 0.10}$ [14]

where k' is a system and temperature dependent constant.

The data from Table I and III for k_a', k_a and (Fe^{3+}/Fe^{2+}) are plotted on logarithm scales in Figure 8. The straight lines shown in this figure are described by the regression equation:

-For reduction:
$\log k_a' = -5.78 + 1.09 \log (Fe^{3+}/Fe^{2+})$ [15]

-For oxidation :
$\log k_a = -8.22 - 1.26 \log (Fe^{3+}/Fe^{2+})$ [16]

The slopes of both plots are close to 1. This dependence is in apparent accord with a reaction mechanism for the formation /dissociation of CO_2 at the surface of low-iron containing slags to involve the transfer of a single charge, compared to the double charge for high iron containing slag [1-5].

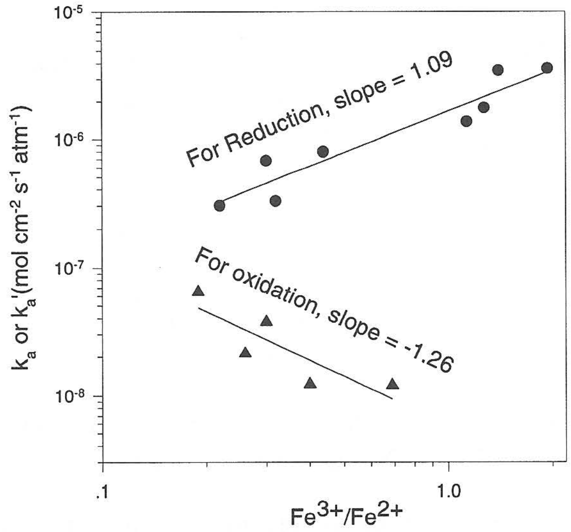

Fig. 8. Dependence of the apparent rate constant on the equilibrium Fe^{3+}/Fe^{2+} in the CaO-MgO-SiO_2-10% FeO_x at 1345 °C.

3.4 Effect of Temperature

A series of experiments of the reduction of slag 28.9% CaO - 54.5% SiO_2 - 7.2% MgO containing about 10 wt% Fe_2O_3 was carried out in the range of temperatures of 1244 - 1500 °C. The slag was first pre-equilibrated in CO_2/CO of 40 and then reduced by a gas mixture of CO_2/CO of 10. The results are plotted in Figure 9. It is evident that temperature has a pronounced effect on the apparent rate constant. According to these results for a given oxygen activity of the slag (at $a_o = 16.9$), the value of k_a increases by about a factor of two for every 100 °C rise in temperature.

The observed temperature dependence on the kinetics of the surface reaction follow the Arrhenius expression given by:

$$k_a' = k_a^o \exp(-E_A/RT) \qquad [17]$$

where E_A is the activation energy, R is the gas constant.

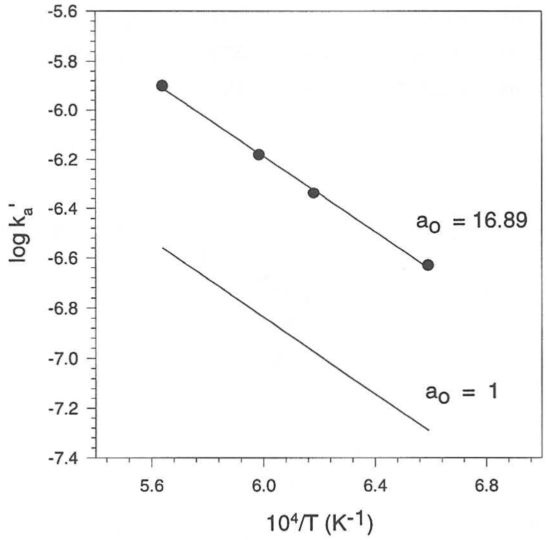

Fig. 9. Arrhenius plot of the apparent rate constant for CO_2/CO ratio of 1 and 16.89.

The activation energy for this gas-slag reaction in chemically controlled region is about 147 kJ/mol (35 kcal/mol). This value is similar to those obtained for the rate of dissociation of CO_2 on low-iron containing slag[5]. The dependence of apparent rate constant on temperature at unit oxygen activity extrapolated from Equation [6] can be described by the following equation:

$$k_a^o = \exp(-35090/RT - 5.17) \text{ (mol cm}^{-2}\text{ s}^{-1}\text{ atm}^{-1}\text{)} \qquad [18]$$

On the basis of the results obtained in this work, the kinetic equation of the reaction of Fe_2O_3 reduction from slag by CO can be written in the following form:

$$r = \exp(-35090/RT - 5.17)(p_{CO}\, a_o^{0.53} - p_{CO2}\, a_o^{-0.47}) \quad \text{(mol cm}^{-2}\text{ s}^{-1}\text{)} \qquad [19]$$

4. CONCLUSIONS

Kinetic measurements of $CaO\text{-}MgO\text{-}SiO_2$ slags containing about 10 wt% FeO_x by blowing a stream of $CO_2\text{-}CO$ gas on a thin layer of slag were made at temperatures in the range of 1244 to 1500 °C. These experiments were carried out under conditions where mass transfer in the gas or slag phase was not the rate controlling step and the results showed that :

- The rate of reduction and oxidation of iron oxide on the surface of slag depends on the oxidation state of the slag. In particular, for reduction, the initial rate increases with increasing oxygen activity in the melt. For oxidation, the initial rate decreases with increasing oxygen activity of the melt.
- The reduction reaction of the slag in Ar gas and in pure CO_2 gas indicated that, at high oxidation state of the slag, the rate of oxygen evolution from the melt may be significant.
- The apparent activation energy was about 147 kJ/mol (35 kcal/mole) and the reduction rate can be expressed as:

$$r = \exp(-35090/RT - 5.17)(pCOa_o^{0.53} - pCO_2\, a_o^{-0.47}) \quad \text{(mol cm}^{-2}\text{ s}^{-1}\text{)}$$

The rate of formation/dissociation of CO_2 at the gas/slag interface was most likely to be the rate controlling step under the experimental conditions employed. The dependence of the apparent first order rate constant on the Fe^{3+}/Fe^{2+} ratio in the low iron oxide containing slags was in accord with a reaction mechanism which involves single charge transfer between the Fe^{3+}/Fe^{2+} and adsorbed CO_2 species at the interface.

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