Kinetics of Oxygen Evolution from Fe_2O_3-CaO-SiO_2-Al_2O_3 Slags

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ABSTRACT

Kinetics of evolution of oxygen from Fe_2O_3-containing slags into an impinging inert gas (argon) have been studied at 1370°C. Slags of CaO-SiO_2-Al_2O_3-Fe_2O_3 were used with $CaO/SiO_2=1.06\pm0.01$, 19~26wt% Al_2O_3 and 3~21% iron oxide (in Fe_2O_3). The slag was stirred by a rotating alumina disc at the surface at 900rpm and purified argon was impinged on to the slag surface at 4L/min. Reaction rates were determined from the variation of ferrous concentrations with time and were found to be controlled by mass transfer steps in both the gas and the slag.

1. INTRODUCTION

There have been numerous studies on kinetics of various gas-slag reactions involving reactive gases such as CO and CO_2.[1] Most previous studies were focused on fairly reduced slags with the oxygen potential close to the formation of metallic iron and little has been known for less reduced, particularly oxidised slags. There is now a need to fill this gap in view of the growing interests in new bath smelting processes for iron ore, which may involve gas-slag reactions with the slag being less reduced or even oxidised locally when a feed rich in Fe_2O_3 is used.

The behaviour of the oxidised slags (high in ferric to ferrous ratios) in gas-slag reactions is somewhat different from that of the reduced slags. For example, when an oxidised slag is exposed to argon, the dissociation of ferric oxide:

$$2(Fe_2O_3)_{slag} = 4(FeO)_{slag} + O_2 \qquad (1)$$

may take place spontaneously. This reaction may be referred to as evolution of oxygen since oxygen is released from the slag not due to a reducing gas but the existence of an oxygen potential gradient between the slag and the gas. As such, this reaction is fundamentally important for oxidised slags, serving as a background reaction for redox reactions involving reactive gases.

The possible involvement of the oxygen evolution in redox reactions was first noticed by Kukhtin and Smirnov[2,3] in their studies on the reduction of Fe_2O_3 in a $40CaO$-$40SiO_2$-$20Al_2O_3$ (by weight) slag by 4~50%CO-Ar at around 1400°C. They found the reaction was approximately first order in pCO. However, extrapolation of the observed rates to pCO=0 did not pass through the origin, suggesting continued reduction in pure argon. Further, the extrapolated zero pCO rates increased with increasing iron oxide. These predicted reduction rates in pure argon were attributed to the dissociation of Fe_2O_3 under argon. Unfortunately, no direct measurement was made of the rate of this reaction.

Oxygen evolution from oxidised slags has also been observed in a recent study on rates of dissolution of Fe_2O_3 and FeO pellets into a $40CaO$-$40SiO_2$-$20Al_2O_3$ (wt%) slag at 1450°C by Ozturk and Fruehan[4]. In a slag with no external stirring, the rates of dissolution of Fe_2O_3 pellets were found to be faster than FeO pellets due to the oxygen evolution which increased the heat and mass transfer.

In the present study, kinetics of evolution of oxygen from Fe_2O_3 containing slags have been studied under the conditions of enhanced mass transfer in both the gas and the slag. The slag composition is close to bath smelting slags so results could be applicable to relevant gas-slag reactions in these processes.

2. EXPERIMENTS

The experimental arrangement is shown in Fig.1.

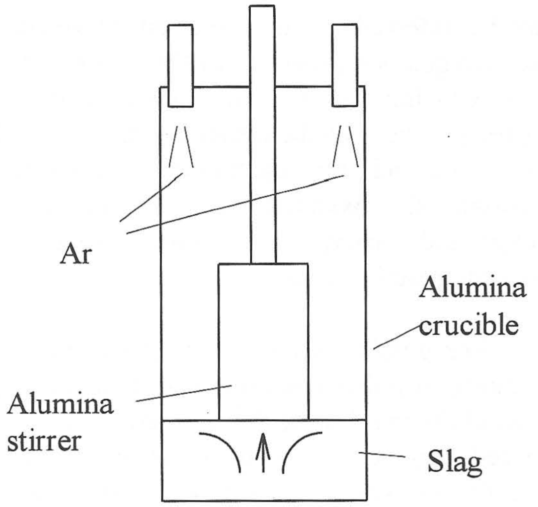

Fig. 1. Experimental arrangement.

Synthetic slags were prepared from reagent grade chemicals $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3, which were weighed according to proportion ($39CaO$-$41SiO_2$-$20Al_2O_3$) + Fe_2O_3. The slag was held in an alumina crucible of 37mm I.D. The actual composition of molten slag during rate measurements was probably close to alumina saturation, with Al_2O_3 varying from 19 to 26wt% corresponding to total iron oxide from 3 to 21% (in Fe_2O_3) while the CaO/SiO_2 ratio remained constant at 1.06 ± 0.01. The variation of alumina content was expected to have little effect on redox equilibria and kinetic results.

The weight of the slag was 55g initially and the depth of the slag bath was about 18mm. The temperature of the slag was controlled at 1370°C in all experiments.

Two gas jets (alumina tubes of 4mm I.D.) were symmetrically located inside the mouth of the crucible as shown in Fig.1. Argon was purified and then delivered on to the slag surface at a total flowrate of 4 L/min. The slag bath was stirred by a rotating alumina disc of 20mm diameter positioned at the surface and all experiments were carried out at a stirring rate of 900 rpm.

The procedure of the experiments was as follows. The slag was equilibrated with bubbling air for half an hour and then the stirring and gas delivery apparatus were set up (Fig.1). The slag bath was stirred for 3 mins and the first sample was taken by inserting an alumina tube into and withdrawing it immediately from the slag bath. Rate measurements began by introducing argon. Five to six more samples were taken at desired intervals. All samples were analysed later for ferrous and total iron by the conventional titration method. Sampling caused an interruption in stirring and argon flow of about 1 minute each and reduced the total weight of the slag bath from 55 to about 50 grams during the experiment.

3. RESULTS

Measurements are summarised in Fig. 2 in the form of variation of ferrous concentrations as a function of time. Based on known experimental conditions, rates of evolution of oxygen may be estimated from the slopes of the tangent lines drawn to these curves.

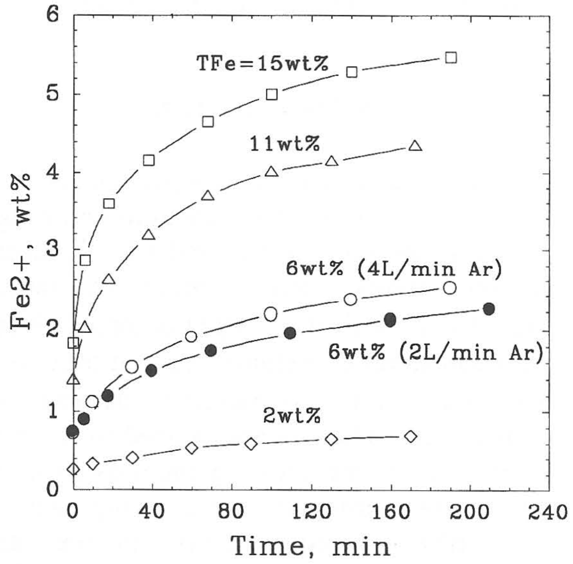

Fig. 2. Experimental measurements of ferrous concentrations at 900rpm and 4L/min argon.

At a given gas flowrate (4L/min), the observed rate increased with increasing total iron concentration as shown by the results for four experiments designated by open symbols in Fig.2. For a given slag (6wt% total iron), a decrease in argon flowrate from 4L/min to 2L/min caused a decrease in the rate as shown in Fig. 2.

4. DISCUSSIONS

The overall reaction of oxygen evolution may involve the following three major steps: (1) the mass transfer of ferric oxide from the bulk to the surface of the slag, (2) chemical reaction at the gas-slag interface, and (3) the mass transfer of reaction products (oxygen in gaseous phase and ferrous oxide in the slag) to the respective bulk phases. To meet the requirement of charge balance, the rate of the mass transfer of ferric oxide to the surface should be equal to that of ferrous oxide in the opposite direction.

4.1 Mass Transfer in Slag

The rate of the mass transfer in the slag (in g-Fe^{2+}.cm^{-2}.min^{-1}) may be conveniently expressed in terms of ferrous concentrations:

$$\frac{W}{100A}\frac{dC_2}{dt} = k_{ms}(C_2^* - C_2) \qquad (2)$$

where W is the weight (g) of the slag, A is the reaction area (cm^2), k_{ms} is the mass transfer coefficient in g-Fe^{2+}.cm^{-2}.min^{-1}.$wt\%^{-1}$, and C_2 and C_2^* are the ferrous concentrations ((Fe^{2+}) in wt%) in the bulk slag and at the slag surface, respectively.

The mass transfer in the slag under the present experimental arrangement was studied based on the measurements made of the rates of reduction of the same slags with a gas mixture of H_2O-H_2 ($H_2O/H_2 \approx 1$), which was delivered from a single gas jet at flowrates of 3.2~3.5L/min. The rate data were found to follow Eq.2 if the ferrous concentration at the surface was assumed to be at equilibrium with the H_2O-H_2 mixture. This is shown in Fig.3 in which the rate data for the 6%Fe slag under varying stirring rates and gas compositions were plotted in the integrated form of Eq.2. Within the experimental uncertainty, linear dependence was observed over a wide range of the bulk ferric to ferrous ratios (6 to 0.1). It was found that the derived rate constants were approximately proportional to the square root of the stirring rate and a 50% dilution with argon did not seem to have a significant effect (Fig.3). These observations suggest that rates of the interfacial reaction and the mass transfer in the gas are comparatively very fast and the overall rates are predominantly controlled by the mass transfer in the slag in these rate measurements.

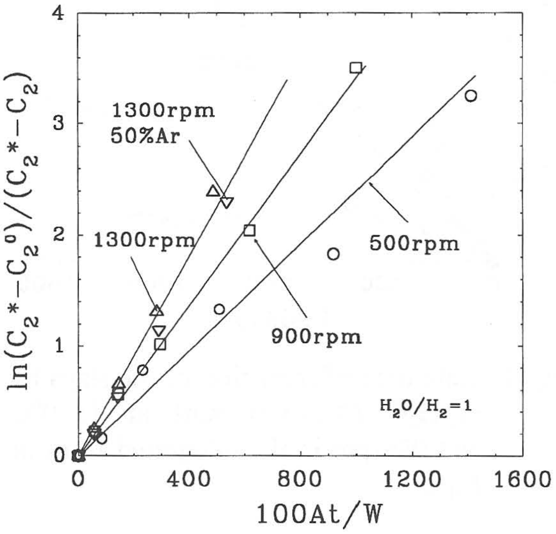

Fig. 3. Rate data of reduction of the 6%Fe slag by H_2-H_2O (3.2~3.5L/min) or H_2-H_2O-50%Ar (3.5L/min), at 1370°C, presented in the integrated form of Eq.2.

At a given stirring rate of 900rpm, the derived mass transfer coefficients, k_{ms}, were found to increase with increasing iron oxide content in the slag as shown in Fig.4 by an increase in the slope. The relationship may be closely described by

$$k_{ms} = (0.3 + 0.514\ C) \times 10^{-3} \qquad (3)$$

where C is the total iron concentration, (Fe^{2+})+(Fe^{3+}) in wt%.

Based on these k_{ms} values and the observed rates (the left hand side of Eq.2), estimated from the slopes of the tangent lines drawn to the curves in Fig.2, the corresponding surface concentrations can be estimated by Eq.2. The results will be shown later.

4.2 Mass Transfer in Gas

Since the oxygen partial pressure in argon is negligibly low, the rate of the mass transfer in the gas can be approximately described by

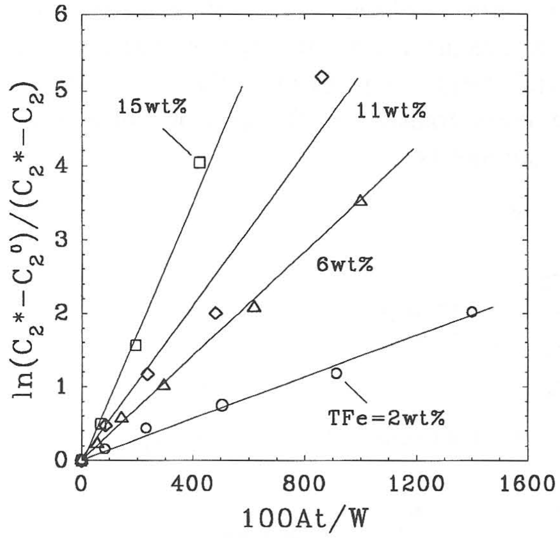

Fig. 4. Rate data of reduction of the slags by H_2-H_2O (3.2~3.5L/min) at 1370°C and 900rpm in the integrated form of Eq.2.

$$\frac{W}{100A}\frac{dC_2}{dt} = k_{mg}pO_2^* \qquad (4)$$

where pO_2^* is the oxygen partial pressure at the surface and k_{mg} is the mass transfer coefficient in the gas in g-Fe^{2+}.cm^{-2}.min^{-1}.atm^{-1}.

The redox equilibria for the present slag could be expressed[5] as

$$\frac{pCO_2}{pCO} = 78.6 \times \left(\frac{C - C_2}{C_2}\right)^{2.22} \qquad (5)$$

If the chemical reaction at the surface is very fast so the oxygen is in equilibrium with the slag surface, the oxygen partial pressure could be expressed by

$$pO_2^* = 8.03 \times 10^{-6}\left(\frac{C - C_2^*}{C_2^*}\right)^{4.44} \qquad (6)$$

Substituting the above into Eq.4 yields

$$\frac{W}{100A}\frac{dC_2}{dt} = k'\left(\frac{C - C_2^*}{C_2^*}\right)^{4.44} \qquad (7)$$

where $k'=8.03x10^{-6}$ k_{mg}. Therefore, if the assumption of a fast interfacial reaction is correct, the observed rate would be proportional to the surface ferric to ferrous ratio raised to a power of 4.44.

In Fig.5, the observed rates are plotted, in an appropriate form according to Eq.7, as a function of the surface concentrations estimated by Eq.2. Within the experimental uncertainty, the observed rates show a linear dependence on the surface ferric to ferrous ratio raised to a power of 4.44 and, furthermore, the slopes appear to be solely dependent on the gas flowrate.

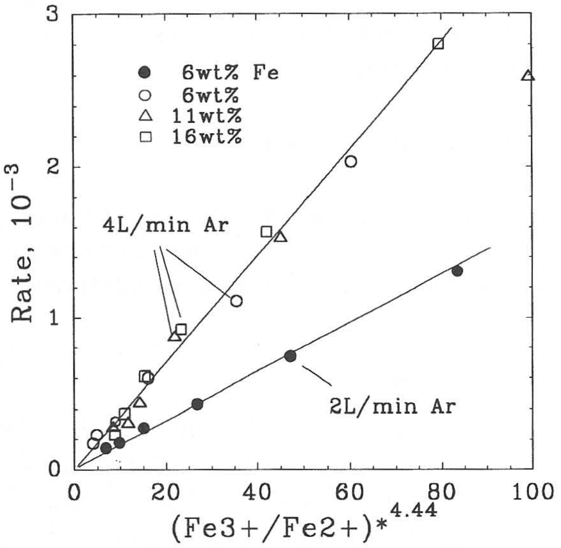

Fig. 5. Observed rates (the left hand side of Eqs.2 and 4 in g-Fe^{2+}.cm^{-2}.min^{-1}) as a function of the estimated surface concentrations.

4.3 Rate Controlling Mechanism

The above observations are consistent with a rate controlling mechanism of fast interfacial reaction and slow mass transfer processes. The overall rates are controlled by the two consecutive mass transfer processes in the slag and the gas with the surface concentrations being determined by the redox equilibria.

Mathematically, the variation of the slag composition is fully described by the two simultaneous mass transfer equations (Eqs.2 and 4), combined with redox equilibria (Eq.6) at the surface. These differential equations may be solved numerically. Of all the coefficients contained in Eqs.2 and 4, only k' is not known. Using the value derived from the slopes in Fig.5 as the starting value, the variation of ferrous concentrations during the experiment was calculated numerically and compared with experimental measurements. The k' values were then adjusted until the best estimate was obtained.

Calculated results are shown in Fig.6 in comparison with the experimental measurements. The agreement is good. The gas mass transfer coefficients derived from the best values for k' are 41 and 20 cm/sec at argon flowrates of 4 and 2 L/min, respectively. They are in broad agreement with those (30 and 18cm/s) predicted by the empirical Taniguchi relationship[6] which was established for the gas mass transfer in a gas impinging system which has a central single jet blowing gas on to a melt surface.

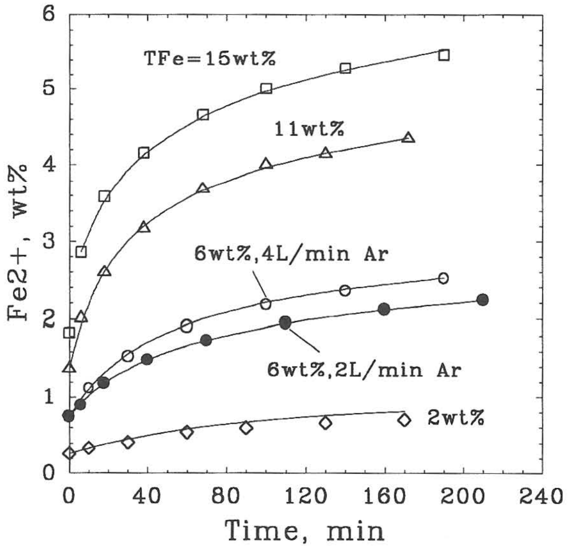

Fig. 6 Comparison of model calculations (curves) with measurements (points).

5. CONCLUDING REMARKS

The overall rate of evolution of oxygen was found to be controlled by mass transfer processes in both the gas and the slag under the conditions of enhanced mass transfer in both phases. Since it is difficult to greatly further increase the mass transfer in the bulk phases, this rate limiting mechanism may be broadly applicable to practical bath smelting processes or laboratory scale research involving ferric oxide containing slags.

For example, the rates of oxygen evolution predicted by Kukhtin and Smirnov[2,3] in their studies mentioned earlier are more than an order of magnitude lower than the observed rates in the present study under comparable conditions. Mass transfer restrictions should also apply and the lower rates are probably due to a much lower rate of the mass transfer in a stagnant slag bath in their experiments.

ACKNOWLEDGEMENT

The authors acknowledge the support of this work by The Broken Hill Proprietary Company Ltd.

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