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A comparison of the kinetics of the CO-CO_2 reaction with steelmaking and copper making slags

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The reaction between carbon and slags is of significant importance in direct smelting of iron ores, EAF slag foaming and copper slag cleaning processes. This reaction is known to occur via gaseous intermediates and it is important to have fundamental data to understand the relative importance of each reaction step. In this study, the rate of CO_2 dissociation on different slag surfaces is measured using an isotope exchange technique. It was found that increasing iron oxide content up to 30 wt per cent does not have a significant effect on the rate constant while increasing from this limit, increases the rate constant dramatically. Activation energy of CO_2 dissociation on slags of unit basicity and different iron oxide contents is in the range of 180±40 kJ/mol. It is found that rate constant dependence on oxygen potential in the slag phase is increasing with iron oxide concentration. In the case of copper making slags, the influence of copper oxide is found to increase the magnitude of apparent rate constant, while decreasing the activation energy considerably.

Key words: Gas-slag reaction, CO_2 dissociation, copper slag, kinetics, isotope exchange

Introduction

The reaction of iron oxide in the liquid state with solid carbon or carbon dissolved in iron has had increasing attention paid to it in recent years. The reaction is the basis of iron or semi-steel production in the new generation of ironmaking processes, also called 'Direct Smelting'. The reaction also plays a major role in increasing the efficiency of the electric arc furnace by slag foaming. In addition, in modern copper making processes, at the 'slag cleaning' stage, reduction of magnetite in the slag with carbon is employed to lower viscosity of slag. With more fluidity, separation of entrapped matte and metal from slag is facilitated. Because of the practical importance of the reaction, a considerable number of studies have been reported on both fundamentals and applied aspects of reaction of iron oxide in the liquid state with carbon. It has been demonstrated[1–5] that the reaction proceeds through an intermediate gas layer around carbon particles. This layer is mostly comprised of CO and CO_2. The overall reaction involves the following individual steps in series[1–4]:

Diffusion of FeO_x (Fe^{+2}/Fe^{+3} and O^{-2} ions) from the bulk slag to the slag-gas interface;

Interfacial chemical reaction at the slag-gas interface,

$$\left(Fe^{2+},O^{2-}\right)+CO=Fe+CO_2 \qquad [1]$$

$$\left(2Fe^{3+},3O^{2-}\right)+CO=\left(2Fe^{2+},2O^{2-}\right)+CO_2 \qquad [2]$$

Diffusion of CO_2 away from the slag-gas interface toward the gas-carbon interface.

Chemical reaction at the carbon-gas interface,

$$CO_2+C=2CO \qquad [3]$$

Diffusion of CO away from the gas-carbon interface to the gas-slag interface.

Numerous kinetics studies have been carried out on the overall reaction rate as well as individual reaction steps. Inconsistencies have been observed among the results of different investigations for the values of reaction rate, controlling steps and mechanism of reaction[5–8,10].

In the present work, the rate of dissociation of CO_2 on different types of slag has been studied. The effect of iron oxide content, oxidation state and temperature, on the rate constant has been investigated. In addition, the effect of copper oxide addition to the slag has been examined.

Experimental

Isotope exchange method

In this work, the isotope exchange method has been employed for the measurements of rate of reaction. Many studies have been made to measure the interfacial rate of CO_2 dissociation on the surface of different metals[11–12] and slags[13–17] by isotope exchange method. The overall exchange reaction is given by:

$$^{*}CO_2+CO=CO_2+^{*}CO \qquad [4]$$

where * symbol, represents the labelled carbon. This can be either the radioisotope ^{14}C or stable isotope ^{13}C. Equation [5] was employed by Cramb and Belton[12] to determine the rate constant (k_a) of CO_2 dissociation when $^{14}CO_2$ is the tracer isotope;

$$\frac{\dot{V}}{ART}\frac{1}{1+\beta}\ln\left[\frac{1}{1-P_{14_{CO}}/\left(P_{13_{CO}}\right)eq}\right]=k_a \qquad [5]$$

where A is the reaction area; T, absolute temperature; β, the equilibrium CO_2/CO ratio; $\dot{V}$, the volume flowrate of the gas mixture; $P_{14_{CO}}$, the partial pressure of tagged CO in the reacted gases and $(P_{14_{CO}})_{eq}$ is the partial pressure of labelled CO if complete equilibrium were to be achieved.

In the present study, the stable isotope ^{13}C ($^{13}CO_2$) was employed as the tracer isotope. By taking full account of the natural abundance of ^{13}C, Equation [5] was modified as follows:

$$\frac{\dot{V}}{ART}\frac{1}{1+\beta}ln\left[\frac{1-P^{\circ}_{13_{CO}}/\left(P_{13_{CO}}\right)_{eq}}{1-P_{13_{CO}}/\left(P_{13_{CO}}\right)eq}\right]=k_a \qquad [6]$$

where all meanings for terms in Equation [5] are valid for this equation with the new term $\overset{\circ}{P}_{13_{CO}}$ being the partial pressure of ^{13}CO in the inlet gases, i.e. the partial pressure of natural ^{13}CO.

Experimental procedure

A slag sample weighting 0.5 to 1 gram was placed in a platinum, alumina or zirconia crucible in the vertical resistance heated tube furnace. This arrangement is shown in Figure 1. Once the desired temperature was achieved, CO-CO_2 gas mixture was passed over the slag. Gas flowrates were adjusted to yield desired CO_2/CO ratio and flow rate. The overall gas flowrate was kept high enough to be in the regime of interfacial chemical control. Each slag sample was equilibrated for at least 1 hour under controlled CO_2/CO ratio then labelled gas was introduced. The labelled gas contained 10 mol per cent $^{13}CO_2$, but was diluted on mixing. An Isoprime isotope ratio mass spectrometer (Micromass) was employed to measure the concentration of labelled species in both ingoing and outgoing gas samples.

Results

CaO-SiO_2-FeO_x Slags

Experiments were conducted to measure the oxidation rate of CaO-SiO_2-FeOx slags with unit basicity (CaO/SiO_2=1.0 molar) and iron oxide content varying from zero to 90 wt per cent. The effect of oxidation state of the slag (fixed by the CO_2/CO ratio and temperature) on the magnitude of rate constant was examined for each slag composition.

Effect of iron oxide content

Figure 2 shows the dependence of apparent rate constant, k_a, on the iron oxide content in the slag. A very sharp increase in the k_a is seen with 'FeO_x' content increasing above 30 and up to 90 per cent. Data from several other studies are included for comparison.

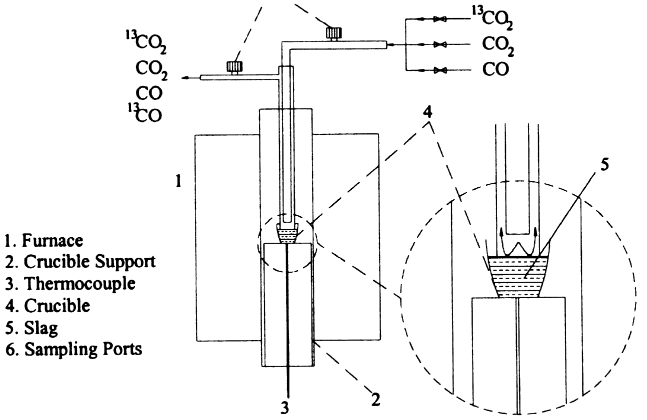

Figure 1. Schematic diagram of experimental apparatus

Effect of oxidation state of the melt

Dependence of k_a on the applied CO_2/CO ratio for some of the studied slags is presented in Figure 3. It is seen that log (k_a) decreases linearly with increasing log(CO_2/CO).

Effect of temperature

Figure 4 shows the temperature dependence of k_a with CO_2/CO=1.0 for slags of unit basicity and different iron oxide contents. Activation energy of 180 ± 40 kJ/mol is obtained for different iron oxide content.

SiO_2-Al_2O_3-FeO_x -(Cu_2O) Slags

To determine the effect of copper, rate constant measurements at varying CO_2/CO and temperature were

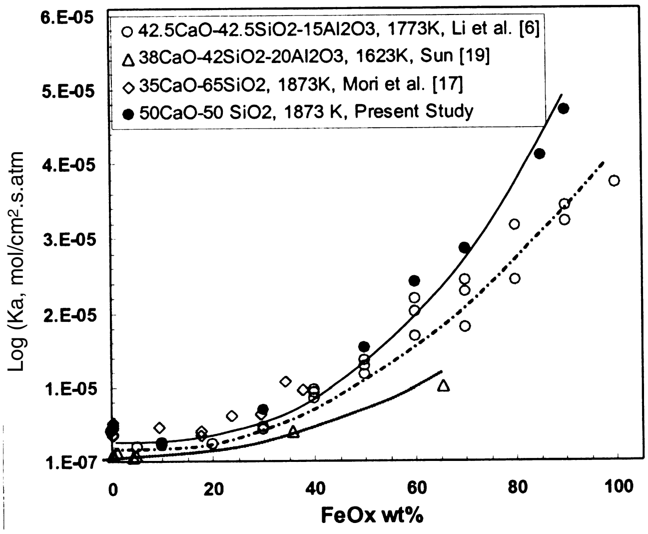

Figure 2. Apparent rate constant as a function of FeO_x content for slags equilibrated with CO_2/CO =1.0

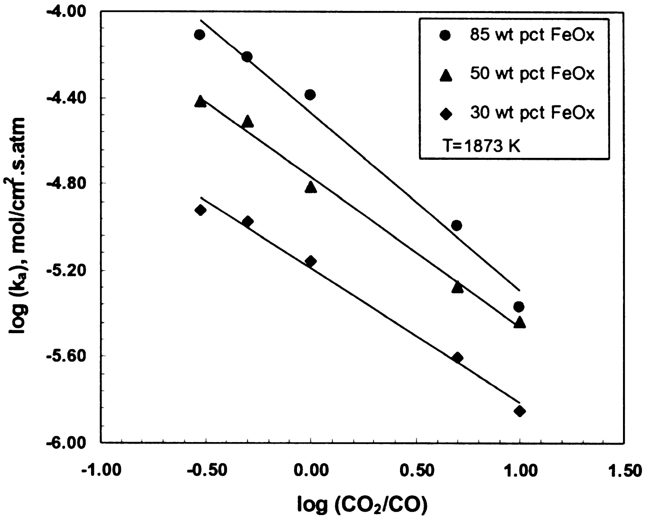

Figure 3. Apparent rate constant as a function of CO_2/CO ratio for different slags at 1873 K

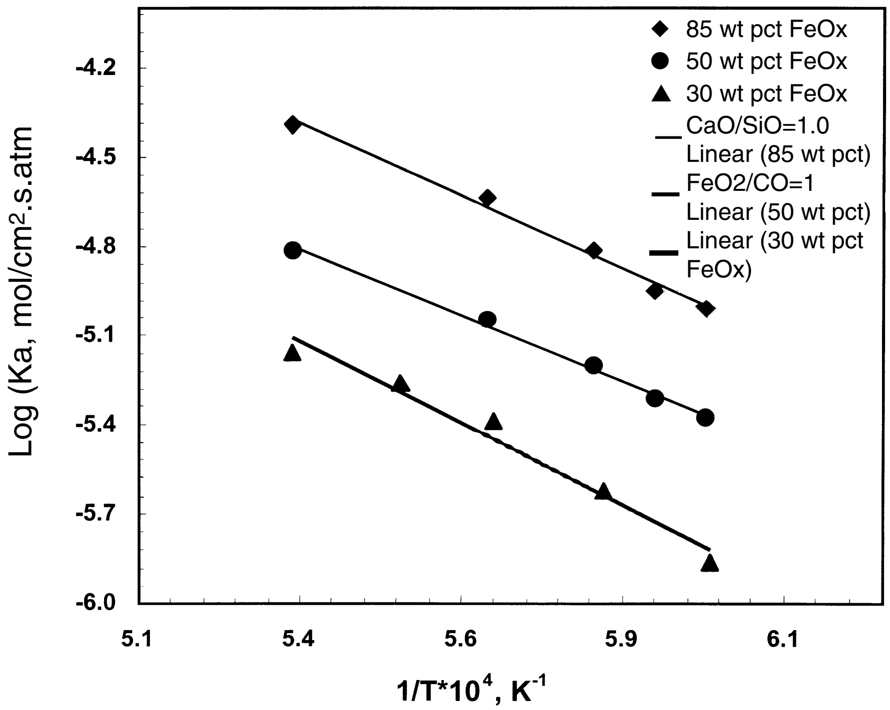

Figure 4. Arrhenius plot of the apparent rate constant measured at CO_2/CO =1.0 for some slags

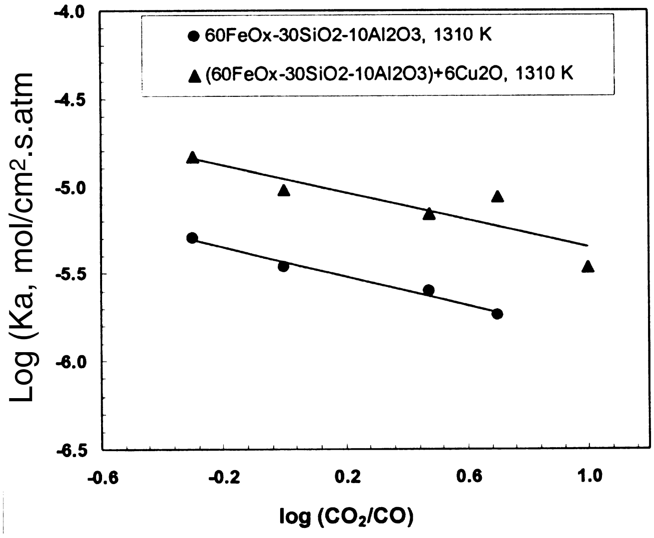

Figure 5. Dependence of apparent rate constant on CO_2/CO for two types of slags, with copper and without copper, both at 1583 K

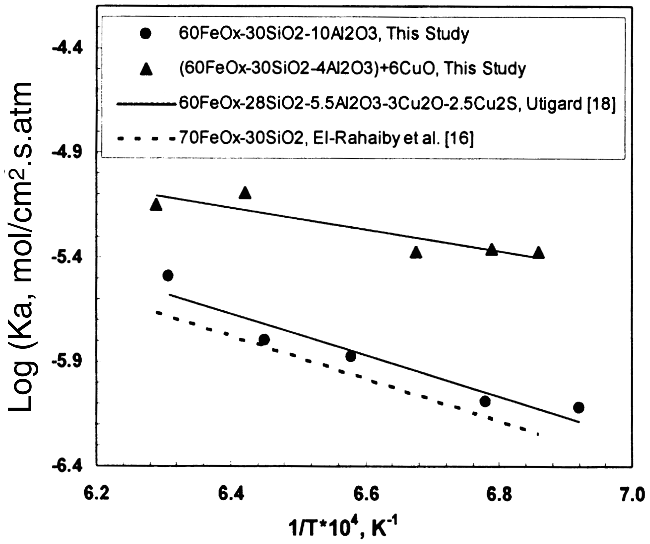

Figure 6. Arrhenius plot of the apparent rate constant, measured at CO_2/CO =1.0

conducted on two slags: copper free slag with 60 wt per cent FeO_x, 30 wt per cent SiO_2, 10 wt per cent Al_2O_3 and a slag, with the same wt ratios of FeO_x to SiO_2 to Al_2O_3, plus 6 wt per cent Cu_2O. The dependence of k_a on CO_2/CO ratio for both slags is provided in Figure 5. An increase in the k_a is seen while the slope of lines remained essentially constant.

Results of present and previous studies on temperature dependence of k_a are presented in Figure 6. Addition of copper to slag has lowered the activation energy from 190 to 100 kJ/mol.

Discussion

Rate of oxidation of iron oxide containing slags

Effect of oxidation state of the slag

The relationship between the rate constant of CO-CO_2 reaction with slags and the oxidation state of slag can be simply expressed as

$$k_a = k_a^{\circ}(a_O)^{-n} \qquad [7]$$

where a_O is the imposed CO_2/CO, k_a° is temperature dependent constant for any slag composition and n characterizes the degree of dependence of rate constant to the oxidation state of the slag.

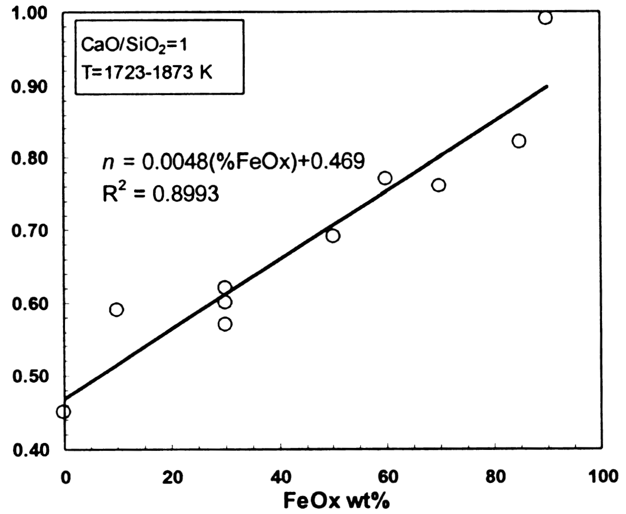

Figure 7. Dependence of n on the iron oxide content in the melt with $CO_2/CO=1.0$

Variation of *n* for different iron oxide content is provided in Figure 7. Despite small discrepancies, it is shown that increasing FeO_x from zero to 90 wt per cent, increases *n* from approximately 0.5 to 1.0.

While many investigators[13,16–17] have found an inverse relationship ($k_a = k_a^\circ(a_O)^{-1}$) for the rate of reaction on iron oxide rich or pure iron oxide condense phases, Sun[19] showed that the first order rate constant for CO_2 dissociation on CaO-SiO_2-Al_2O_3 slags containing about 1 per cent FeO_x decreased with a_O according to relationship $k_a = k_a^\circ(a_O)^{-0.5}$. El-Rahaiby *et al.*[16] have also shown that for an equimolar CaO-SiO_2-FeO_x slag, $k_a = k_a^\circ(a_O)^{-0.75}$). It is thus apparent that, as FeO_x decreases, k_a dependence on a_O decreases. From results of this study, as seen in Figure 7, it may be concluded that the rate constant dependence on the state of oxidation is variable depending on the total iron oxide content in the slag. Increasing the iron oxide content of the slag, increases the value of *n* to unity for iron-rich slags.

A mechanism, involving transfer of two negative charges (electrons) to the adsorbed CO_2 would lead us to expect a value of 1 for *n*. For a detailed review, the reader is referred to an article by Sasaki *et al.*[13]. Briefly, based on this mechanism, for a given number of reaction sites, the reaction rate is proportional to the surface concentration of weakly adsorbed CO_2^{2-} ions. The ions are formed through following reaction:

$$CO_{2(ad)} + 2e^- = CO_{2(ad)}^{2-} \qquad [8]$$

The oxidation state of the slag, affects the electronic defect structure, thereby affecting the electrochemical potential of electrons which finally influence the concentrations of CO_2^{2-}. This mechanism explains the value of -1 for *n*. However, it fails to explain the values of *n* less than 1. There are two possible explanations for the deviation of *n* from unity in some slag systems, particularly at low iron oxide contents;

Firstly, if adsorbed ions on the slag surface, are produced in the form of singly charged ions (CO_2^-), instead of doubly charged CO_2 ions, (CO_2^{2-}), value of *n*, should be 0.5 in ideal slags. This value is very close to low-iron content slags. On the other hand, value of *n* in the iron-rich end of diagram, is close to 1. Therefore, it can be explained that increasing the iron oxide content of the slag, the dominant mechanism changes from formation of singly charged to doubly charged CO_2 ions.

The second probable reason for changing the value of *n* with FeO_x content may be variation in the electronic structure of slag with variation in iron oxide content. For pure iron oxide, when doubly charged CO_2 is adsorbed on the surface, the 'ideal value' of *n*=1 is confirmed by this charge transfer model. However, addition of other oxides to the iron oxide can cause variations in its electronic properties thus deviation in the 'ideal' behaviour.

Effect of iron oxide content

Results of present and some of previous studies have been gathered in Figure 2. An exponential trend is observed in all separate studies. Increasing iron oxide content up to approximately 30 per cent does not have a significant effect on the k_a. On the other hand, increasing 'FeO_x' content, from this limit up to 100 wt per cent increases the rate dramatically. The lower temperature studies of Li *et al.*[6] and Sun[19] deviate at higher FeO_x contents. This can be attributed to higher temperature in the present study. Assuming a constant activation energy at different iron oxide contents, the observed divergence of the two sets of data is close to the expected. As seen, the agreement with the study of Mori *et al.*[17] for the experiments conducted at the same temperature as the present work is extremely good.

As noted in previous section, based on charge transfer mechanism, electronic properties of slag can affect the rate of reaction significantly. Several measurements on electrical conductivity of slag[20–23] show that increasing iron oxide content of the slag, increases the electrical conductivity. Li *et al.*[6] gathered data on the electrical conductivity of iron oxide melts and showed that electrical conductivity as a function of FeO_x content is analogous to the variations of k_a. They concluded that electrical properties of slag are most likely to be the reason for such trend in dependence of k_a on FeO_x content.

Effect of copper oxide addition

As shown in Figure 5, addition of 6 wt per cent Cu_2O to the slag at 1583K, increases k_a by a factor of 3, while there *is no change in the CO_2/CO dependency, with a slope of -0.4* for both lines. The effect of copper could be explained in terms of basicity. In general, the apparent rate constant at a given oxygen potential increases with the basicity of the melt[16]. It is reasonable that oxygen transfer is more rapid on a more extensively reduced surface, because of the readier dissociation of CO_2[24]. From thermodynamic data, it is known that Cu^+ has a higher reducibility than Fe^{3+}.

The arguments, whether considered in terms of basicity or extent of reduction, depends on the presence of copper ions in the slag. However, from thermodynamic data, it is expected that in the present work a significant proportion of copper oxide is reduced to copper metal. Therefore, increase in the k_a may have arisen from different phenomena. One possibility is suspension of small copper droplets at the slag/gas interface. Another possible effect is the presence of Cu^+ ions in the slag, as described earlier. At this stage, the role of each phenomenon has not been clarified but an investigation of this is ongoing.

The strong influence of copper on the apparent rate constant is also illustrated in Figure 6. This figure shows again that the reduction rate is more rapid on the surface of a copper slag than on that of copper-free slag. The calculated activation energy is 190 kJ/mole for slag without Cu_2O. However, it is only 100 kJ/mole for slag with Cu_2O

Results of other studies on similar slags are also shown in Figure 6. The activation energy for copper free slag is very close to El-Rahaiby's[16] result (196 kJ/mol) for a slag with a similar composition. Compared with Utigard's[18] results, the biggest difference for the rate constants is 1 order within the experimental temperature range after adding Cu_2O. This might be because that there is 0.5 per cent S in Utigard's slag.

Conclusion

- For CO_2/CO exchange in $CaO\text{-}SiO_2\text{-}FeO_x\text{-}Al_2O_3\text{-}(Cu_2O)$ slags, the rate constant decreases with oxygen potential. This decrease is consistent with a charge transfer mechanism and a rate determining step involving CO_2^{2n-} formation/dissociation where $0.5 \le n \le 1$.
- The rate constant for a given temperature is represented by the equation

$$k_a = k_a^{\circ}\left(\frac{P_{CO2}}{P_{CO}}\right)_{eq}^{-n}$$

for an iron silicate slag with and without copper, n=0.4 for $CaO\text{-}SiO_2\text{-}FeO_x$ slags, and n is a function of total iron oxide content. For a CaO/SiO_2=1 slag, $n = 0.0048(\%FeO_x)+0.469$

- The activation energy was found to be independent of total iron oxide content but was dependent on copper presence in slag. For copper free slags, activation energy was 180kJ/mol. Addition of 6 wt per cent copper oxide, decreased activation energy to 100 kJ/mol.
- For $CaO\text{-}SiO_2\text{-}FeO_x$ slags, the rate constant increases significantly with total iron content, when iron oxide increases from approximately 30 wt per cent.

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References

1. SARMA B., CRAMB A.W., and FRUEHAN R.J. Reduction of FeO in smelting slags by solid carbon: experimental results. *Metall. Trans. B.* vol. 27, 1996, pp. 717–731.
2. SIDDIQI, N., BHOI, B., PARAMGURU, R.K., SAHAJWALLA, V., and OSTROVSKI, O. Slag-graphite wettability and reaction kinetics, part 1 kinetics and mechanism of molten FeO reduction reaction., *Ironmaking and Steelmaking* vol. 27, no. 6, 2000, pp. 437–441.
3. MIN, D.J. and FRUEHAN, R.J. Rate of reduction of FeO in slags by FeO-C drops *Metall. Trans. B.* vol. 23, 1992, pp. 29–37.
4. MIN, D.J., HAN, J.W., and CHUNG, W.S. A study of the reaction rate of FeO in slag by solid carbon, *Metall. Trans. B.* vol. 30, 1999, pp. 215–221.
5. SHEIKHSHAHAB BAFGHI, M., FUKUDA, M., ITO, Y., YAMADA, S., and SANO, M. Effect of CO gas formation on reduction rate of iron oxide in molten slag by graphite, *ISIJ Int.* vol. 33, no. 11, 1993, pp. 1125–1130.
6. LI, Y. and RATCHEV, I.P. Rate of interfacial reaction between molten $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}FeO_x$ and $CO\text{-}CO_2$, *Metall. Trans. B.* vol. 33, 2002, pp. 651–660.
7. JI, F., BARATI, M., COLEY, K., and IRONS, G.A. A kinetic study of carbon injection into electric arc furnace slags, *7th International Conference on Molten Slags, Fluxes and Salts*, Cape Town, South Africa, 25-28 January 2004.
8. STORY, S.R., SARMA, B., FRUEHAN, R.J., CRAMB, A.W., and BELTON, G.R. Reduction of FeO in Smelting Slags: Re-Examination of the Influence of the Gas-Carbon Reaction, *Metall. Trans. B.* vol. 29, 1998, pp. 829–832.
9. MIN, D.J., HAN, J.W., and CHUNG, W.S. A Study of the Reaction rate of FeO in slag by solid carbon, *Metall. Trans. B.* vol. 30, 1999, pp. 215–221.
10. SHALIMOV, M.P., BORONESHKOV, V.N., and LYAMKIN, S.A. Mechanism and kinetics of $FeO\text{-}SiO_2$ melts with carbon, *Russian Metall.*, vol. 3, 1980, pp. 31–34.
11. CRAMB, A.W., GRAHAM, W.R., and BELTON, G.R. The interfacial kinetics of the reaction of CO_2 with nickel. Part1: the $^{14}CO_2$-CO exchange reaction and the influence of sulphur, *Metall. Trans. B.* vol. 9, 1978, pp. 623–629.
12. CRAMB, A.W. and BELTON, G.R. Studies of the interfacial kinetics of the reaction of CO_2 with liquid iron by the $^{14}CO_2$-CO isotopic exchange reaction *Metall. Trans. B.*, vol. 12, 1981, pp. 699–704.
13. SASAKI, Y., HARA, S., GASKELL, D.R., and BELTON, G.R. Isotope exchange studies of the rate of dissociation of CO_2 on liquid iron oxides and CaO-saturated calcium ferrites. *Metall. Trans. B.*, vol. 15, 1999, pp. 563–571.
14. SUN, S. and BELTON, G.R. The effect of surfactants on the interfacial rates of reaction of CO_2 and CO with liquid iron oxide , *Metall. Trans. B.*, vol. 29, 1998, pp. 137–145.
15. SUN, S., SASAKI, Y., and BELTON, G.R. On the interfacial rate of reaction of CO_2 with a calcium ferrite melt, *Metall. Trans. B.*, vol. 19, 1988, pp. 959–965.
16. EL-RAHAIBY, S.K., SASAKI, Y., GASKELL, D.R., and BELTON, G.R. Interfacial rates of reaction of CO_2 with liquid iron silicates, silica-saturated manganese silicates and some calcium iron silicates, , *Metall. Trans. B.*, vol. 17, 1986, 17, pp. 307–316.
17. MORI, M., MORITA, K., and SANO, N. Determination of the rate of CO_2 dissociation on the surface of $CaO\text{-}SiO_2$, $CaO\text{-}Al_2O_3$, $CaO\text{-}SiO_2\text{-}CaF_2$ and $CaO\text{-}SiO_2\text{-}FeO_x$ melts *ISIJ Int.*, vol. 36, no. 6, pp. 624–630.

18. UTIGARD, T., SANCHEZ, G., MANRIQUEZ, J., LURASCHI, A., DIAZ, C., and CORDERO, D. Reduction kinetics of liquid iron oxide-containing slags by carbon monoxide, , *Metall. Trans. B.*, vol. 28, 1997, pp. 821–26.

19. SUN, S. Aspects of the kinetics of reaction of CO_2 and CO with oxide melts, Ph.D. thesis, University of Newcastle, NSW, Australia, 1988.

20. DUCRET, A., KHETPAL, D., and SADOWAY, D.R. Electrical conductivity and transference number measurements of FeO-CaO-MgO-SiO_2 melts. Presented at *Electrochemical Society Meeting*, Philadelphia, May 2002.

21. JIAO, Q. and THEMELIS, N.J. Correlations of electrical conductivity to slag composition and temperature, *Metall. Trans. B.*, vol. 19, 1988, pp. 133–140.

22. NARITA, K., ONOYE, T., ISHII, T., and UEMURA, K. Electric conductivity of CaO-SiO_2-Fe_tO slag, *Tetsu-to-Hagané*, vol. 61, 1975, pp. 2943–51.

23. FONTANA, A., SEGERS, L. TWITE, K. and WINAND, R. Electrical conductivity of ferrous silicate melts from slag cleaning operations, *TMS-AIME* paper selection, paper No. A84-39, 1984.

24. OZAKI, A. Isotopic studies of heterogeneous catalysis, Academic Press, 1977.