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REDUCTION KINETICS BEHAVIOR OF FeO-CaO-SiO$_2$-MgO-Al$_2$O$_3$ MOLTEN SLAG USING SOLID-CARBON

Reduction of FeO-bearing molten slag using solid-carbon, existing in primary slag of blast furnace (BF), consumes much BF energy. It is also a limit for BF efficiency. In this paper, reduction kinetics behavior of FeO-CaO-SiO$_2$-MgO-Al$_2$O$_3$ molten slag (primary slag of BF) was investigated, and the restrictive step of the reaction was identified. It has been found that the reduction process of FeO-CaO-SiO$_2$-MgO-Al$_2$O$_3$ BF slag using solid-carbon is a second-order reaction. And the reduction process is controlled by both diffusion of FeO and gasification reaction of carbon in molten slag. The apparent activation energy of reaction is 342.37 kJ/mol, the diffusion activation energy of FeO in molten slag is 355 kJ/mol, and the gasification reaction activation energy of carbon is 152.98 kJ/mol. Additionally, it is also concluded that reduction rate is influenced by temperature (T), mass fraction of FeO ($w_{(FeO)}$), and basicity (R) of the slag. Moreover, a reduction model of this slag system was established and verified by a series of experiments.

Keywords: kinetics; molten slag; reduction; carbon; blast furnace

1. Introduction

The slagging process of blast furnace (BF) is from the softening/melting of iron ore [1]. The slag, in this step, is so-called primary slag. Actually, the primary slag is consisted of gangue (from iron bearing materials e.g. sinters, pellets and lump ore) and FeO which has not been reduced to Hot Metal (HM) [2-5]. Generally, the portion of FeO in primary slag is 15-20% because FeO and SiO$_2$ have higher reaction rate, forming lower melting point mineral (fayalite) [6]. However, the primary slag will be reduced by coke (solid-carbon) or CO, leading to the FeO content in slag is lower and forming the final BF slag [7]. It is well received that reduction of FeO consumes much carbon (energy) in BF process [8], which certainly involves the reduction of FeO in primary slag. Additionally, the metallurgical properties of BF slag can be addressed via FeO content. For instance, as the FeO content is higher in final BF slag, the losing weight of HM will increase; conversely, the fluidity of BF slag will be worse with much lower FeO content in slag mentioned above [9]. To sum up, the reduction of FeO in primary slag is one of the most essential reactions in BF process, which is also a key point of energy consumption. Therefore, investigation about reduction kinetics behavior of FeO in BF primary slag is very important in aspects of theory and practice needs.

The results, obtained from literatures about the reduction kinetics of slag containing FeO, were usually inconsistent because of different application backgrounds and experimental condi-tions. Min et al. [10] analyzed the reduction kinetics mechanism of FeO bearing molten slag at an experimental condition of smelting reduction slag system (FeO-CaO-SiO$_2$, R = 0.6-0.8) in 1753 K-1783 K. It was confirmed that the restrictive step is carbon gasification reaction with a high proportion of FeO (>30%) and the reaction rate is increasing higher with the addition of FeO in slag. Sarma et al. [11] investigated the reduction kinetics of CaO-SiO$_2$-Al$_2$O$_3$-FeO (FeO>15%, R = 1.34) slag system using a reductant of graphite in 1673K-1723K. Similarly, it was pointed out that the reduction rate accelerates with more FeO content in slag, but not a liner relationship. Philbrook *et al* [12] studied the reduction kinetics of BF slag system (5%FeO-CaO-SiO$_2$-Al$_2$O$_3$, 1703 K-1843 K) with a reductant of carbon-saturated HM in a graphite crucible. They believed that two first-order reactions are conducting in parallel. One appears in slag-HM interface and the other is in slag-graphite interface. However, their theory can hardly explain some of phenomenon in their experiments. And a further research obtained by Tarby et al. [13] proposed that two steps take place in FeO reduction. The first step is forced convection caused by stirring action of CO from the reduction reaction and the second is natural convection. Sasaki et al. [14] investigated the effect of basicity (R) on reduction kinetics of CaO-SiO$_2$-FeO slag system in graphite reductant, it was indicated that the reaction rate constant (k) increases as the R goes up from 0.5 to 0.8.

Summarily, previous studies about the reduction kinetics of FeO bearing molten slag paid more attention to FeO-CaO-SiO$_2$

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slag system and FeO-CaO-SiO$_2$-Al$_2$O$_3$ slag system. However, these slag systems are hardly able to meet the production requirements of BF process nowadays where technology and raw materials conditions are different, especially more and more Al$_2$O$_3$ and MgO content is added in BF. Therefore, it is significant to carry out new investigation after adding MgO and Al$_2$O$_3$ in BF slag system. Moreover, the studies about reduction kinetics of FeO in BF slag were rarely reported. Even if some literatures were fulfilled based on BF slag system, but the basicity of the slag sill maintained in a low level ($R = 0.7$-0.9) and these values in present BF slag are maintaining at a level of 0.9-1.3. Consequently, further studies are still essential.

In this paper, the reduction kinetics behavior of FeO-CaO-SiO$_2$-MgO-Al$_2$O$_3$ molten slag (primary slag of BF) was investigated, and the restrictive step of the reaction was revealed. Furthermore, a reduction kinetics model was established and verified by experiments.

2. Kinetics experiments

2.1. Experimental design

The previous studies about the reduction kinetics of FeO bearing molten slag system were involved much in FeO-CaO-SiO$_2$ slag system and FeO-CaO-SiO$_2$-Al$_2$O$_3$ slag system, And the results were usually of inconsistence due to diverse application backgrounds (e.g. used for smelting reduction or used for BF process) and different experimental conditions (such as temperature, original mass fraction of FeO, and basicity and so on). According to the BF process nowadays, the experiment design is shown as follows. Slag system: FeO-CaO-SiO$_2$-Al$_2$O$_3$-MgO; Basicity ($R = w_{(CaO)}/w_{(SiO2)}$): 0.94, 1.08, 1.22, 1.37; Experimental temperature (T): 1673 K, 1723 K, 1773 K, 1823 K; Original mass fraction of FeO ($w_{(FeO)}$) in primary slag: 5%, 10%, 15%. The details are listed in Table 1.

2.2. Experimental methods

The experiments were conducted in an induction furnace (Fig. 1) with a graphite crucible as reductant and with analytical reagents (CaO, MgO, SiO$_2$, Al$_2$O$_3$ and FeO) as raw materials. The samples (molten slag) were taken out periodically from the graphite crucible (of which outer diameter is 80 mm, inner diameter is 60 mm, and height is 120 mm) to test the FeO content in order to identify the reaction steps.

The experimental details are listed as follows. a) The weighted slag was put into the graphite crucible and the furnace was heated up at the rate of 15°C/min. b) High purity N$_2$ was blasted into the furnace in order to prevent samples from being oxidized. c) FeO was put into furnace after reaching required temperature, and stirred with a rod-like Tungsten (melting point >2000 K) for 30 s at a stirring rate of 1 r/s. d) The samples were sampled out by a similar rod-like tungsten referred to above per

TABLE 1

Details of experimental design

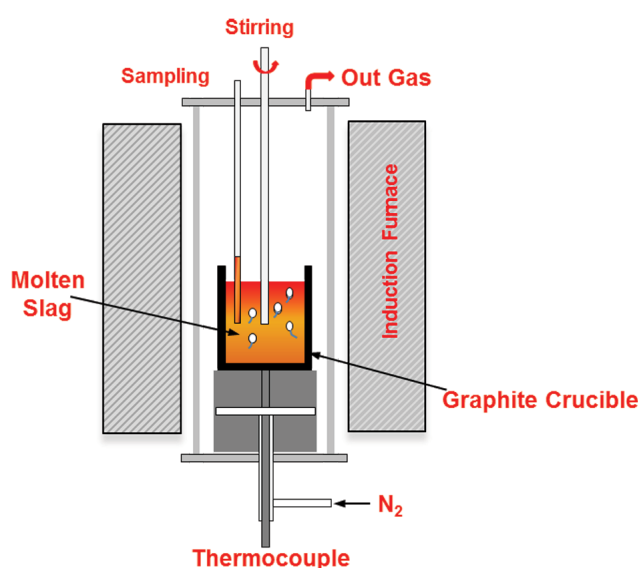| No$_i$ ($i = 1$~9)	R	T/K	$w_{(FeO)}$	Slag Composition			
				$w_{(CaO)}$	$w_{(SiO_2)}$	$w_{(MgO)}$	$w_{(Al_2O_3)}$
1	1.22	1773	10	38.14	31.16	8.10	12.60
2	1.22	1673	10	38.14	31.16	8.10	12.60
3	1.22	1723	10	38.14	31.16	8.10	12.60
4	1.22	1823	10	38.14	31.16	8.10	12.60
5	0.94	1773	10	33.63	35.67	8.10	12.60
6	1.08	1773	10	36.00	33.30	8.10	12.60
7	1.37	1773	10	40.09	29.21	8.10	12.60
8	1.22	1773	5	40.26	32.89	8.55	13.30
9	1.22	1773	15	36.02	29.43	7.65	11.90

Fig. 1. Experimental apparatus

4 min. e) put the hot samples into a vacuum drying oven to dry out and cool down for the further chemical composition analysis via ICP in order to specify the variation of FeO content in experimental slag.

2.3. Reproducible experiment

The reproducible experiments were carried out to improve the accuracy of the results. Both the reduction experiments and chemical analysis of molten slag were repeated for twice. The arithmetic averaged values of the two results were considered as the ultimate results.

3. Experimental results and kinetics analysis

3.1. Experimental results

The variation of FeO content in slag under different conditions (in terms of T, R and $w_{(FeO)}$) is shown in Fig. 2. One can

conclude that the reduction rate of FeO in molten slag accelerates as temperature (T) goes up from 1673 K to 1823 K. Similarly, it maintains a increasing state as basicity (R) goes up from 0.94 to 1.37 and as the $w_{(FeO)}$ increases from 5% to 15%.
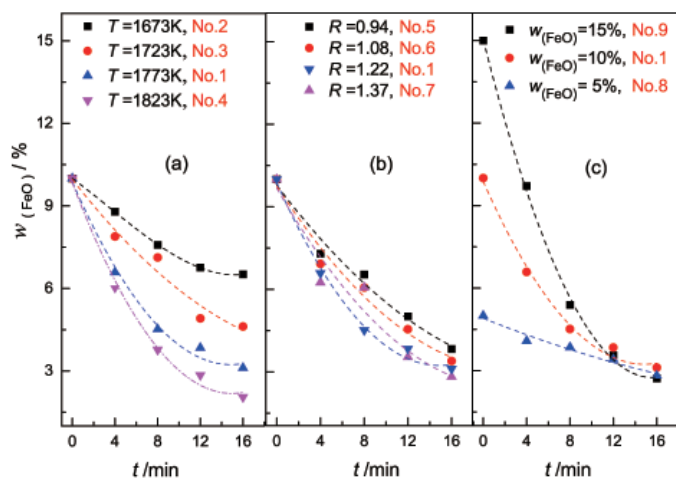

Fig. 2. Reduction curves of FeO in molten slag at various experimental conditions

3.2. Kinetics analysis

The reaction that graphite reduces FeO bearing molten slag is a constant volume reaction in the present work. For lower order reactions in constant volume, the kinetic equations and their integral form are listed in Table 2 [15-16].

TABLE 2

Kinetic equations and integral form of the reaction in constant volume

Reaction order	Reaction rate differential equation	Reaction rate integral equation
Zero-order: A→R	$-dC_A/dt = k$	$C_{A0} - C_A = kt$
First-order: A→R	$-dC_A/dt = kC_A$	$-\ln\dfrac{C_{A0}}{C_A} = kt$
Second-order: 2A→R	$-dC_A/dt = kC_A^2$	$\dfrac{1}{C_A} - \dfrac{1}{C_{A0}} = kt$

The reduction rate of FeO using solid-carbon in molten slag can be proposed as Eq. (1).

$$v = -\frac{dm_{FeO}}{dt} = -m_s\frac{dC}{dt} = k\,A\,C^\alpha \tag{1}$$

Where: v is reduction rate (g/min), m_{FeO} is the FeO weight (g) in slag, m_s is slag weight (g), C is concentration of FeO in slag (%), A is reaction interfacial area (cm^2), k is reaction rate constant (g/cm^2·min), α is reaction order.

Since the losing weight of slag in reduction process is the removing of "O" in "FeO" absolutely and the FeO content in slag referred to here is relatively lower, so $m_s \neq 0$. And the reduction rate of FeO can be expressed as Eq. (2)

$$-\frac{dC}{dt} = \frac{k\,A}{m_s}C^\alpha = k'C^\alpha \tag{2}$$

Where: $k' = kA/m_s$, k' and α referred to here are obtained by experimental results.

Eq. (3), (4) can be obtained by integrating the Eq. (2).

$$-\ln\frac{C}{C_0} = \frac{k\,A}{m_s}t = k't \quad \alpha = 1 \tag{3}$$

$$\frac{1}{1-\alpha}\left(C_0^{1-\alpha} - C^{1-\alpha}\right) = \frac{k\,A}{m_s}t = k't \quad \alpha \neq 1 \tag{4}$$

When $\alpha = 0$ and $\alpha = 2$, the Eq. (4) can be expressed as Eqs. (5), (6)

$$C_0 - C = \frac{k\,A}{m_s}t = k't \quad \alpha = 0 \tag{5}$$

$$\frac{1}{C} - \frac{1}{C_0} = \frac{k\,A}{m_s}t = k't \quad \alpha = 2 \tag{6}$$

The relations between the concentration of FeO and time with various reaction orders ($\alpha = 0$, 1 and 2) are shown in Eqs. (3, 5 and 6). A new function $F(C)$ is defined to represent the concentration of FeO which is on the left side of all these three equations mentioned above. Therefore, Eqs. (3, 5 and 6) can be expressed in the form of Eq.(7).

$$F(C) = \frac{k\,A}{m_s}t = k't \tag{7}$$

The reaction order can be concluded from the $F(C) - t$ curve in Fig. 3 and the slope is k'. From Fig. 3, we can draw a conclusion that the $F(C) - t$ curve has weak linearity as the reaction order (a) is 0 or 1, but approximates a liner relationship as the reaction order is 2. So reduction of FeO-CaO-SiO$_2$-MgO-Al$_2$O$_3$ molten slag system using solid-carbon (graphite) is a second-order reaction.
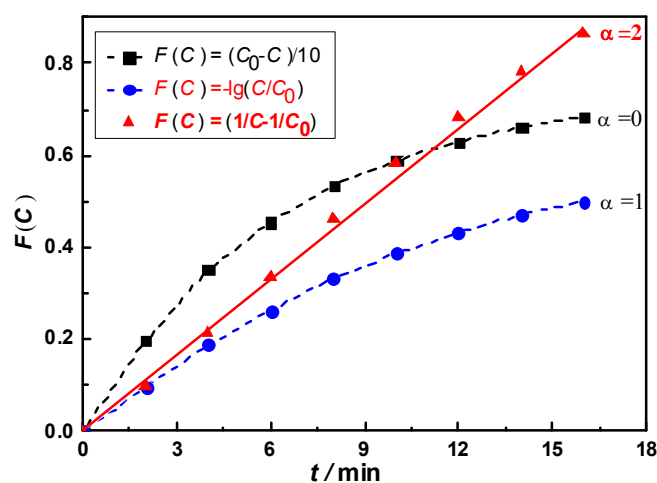

Fig. 3. Determination of the reaction order

The "$(1/C - 1/C_0) - t$" curves (of which the slope is k') at various conditions are shown in Fig. 4. According to the results obtained above, one can see that the reduction rate is influenced

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by T, $w_{(FeO)}$, and R of the molten slag. And the apparent reaction rate constant (k) gets larger as the T, $w_{(FeO)}$, and R are increasing higher, respectively.
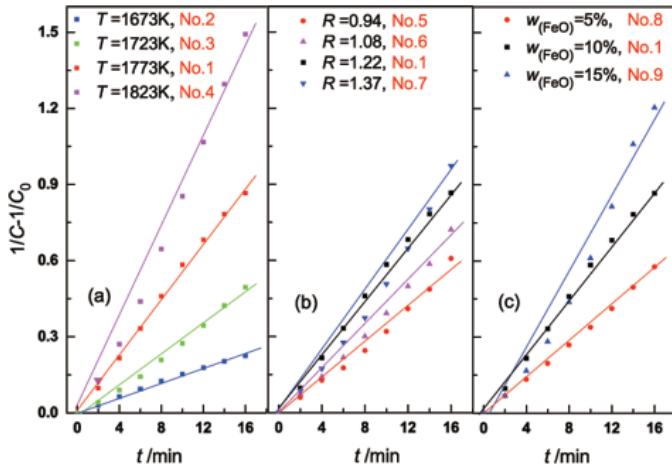

Fig. 4. ($1/C - 1/C_0$) –t curves at various conditions

The relationship of $\ln k - 1/T$ is given in Fig. 5. The linear fitting equation of $\ln k - 1/T$ is listed in Eq. (8). Based on Arrhenius equation, the apparent activation energy of FeO reduction in present experimental slag system is 342.37 kJ/mol.
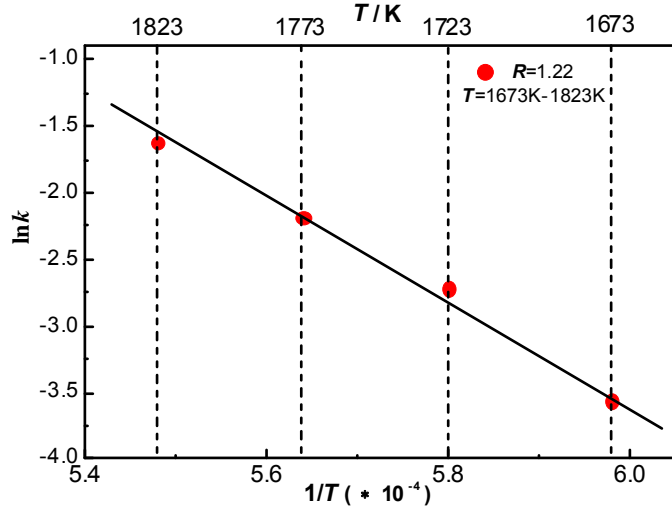

Fig. 5. Relationship of $\ln k - 1/T$

$$\ln k = 21.01 - \frac{342370}{RT} \tag{8}$$

Since the reduction of FeO in experimental slag system is a second-order reaction, the reduction rate can be expressed as Eq. (9).

$$v = -m_s \frac{dC}{dt} = k\, A\, C_{FeO}^2 \tag{9}$$

The reaction interfacial area (A), determined via the contact area between the static molten slag and graphite crucible, is 59 cm^2 and Eq. (10) can be obtained by simplifying the Eq. (8)

$$k = 1.33 \times 10^9 \left[\exp\left(-\frac{342370}{RT} \right) \right] \tag{10}$$

According to Eqs. (9 and 10), the total reduction rate of FeO in molten slag is given in Eq. (11).

$$v = 7.85 \times 10^{10} \left[\exp\left(-\frac{342370}{RT} \right) \right] \cdot C_{FeO}^2 \tag{11}$$

In order to verify accuracy of the model, a series of reduction experiments were carried out at different conditions. The instant reduction rate was obtained based on the changes of FeO content in slag. The comparison between experimental values and calculated values is shown in Fig. 6. From Fig. 6, the calculated values are of agreement well with experimental values at the chosen temperature (1803K, 1773K, 1743K and 1673K). Therefore, this model is of accuracy to describe reduction of FeO in BF primary slag.
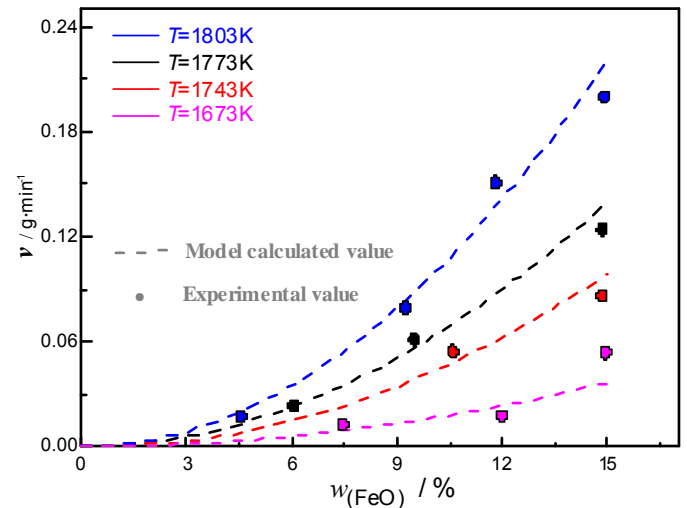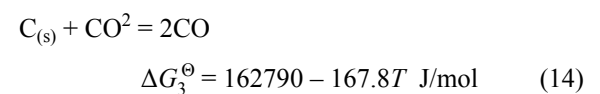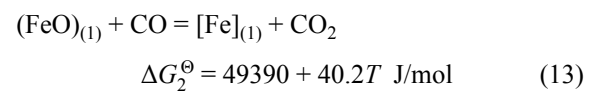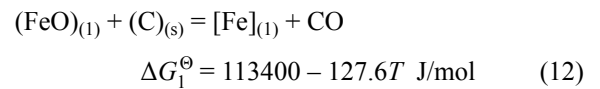

Fig. 6. Comparison between experimental values and calculated values

3.3. Restrictive step

The following reactions are listed in Eqs. (12 to 14) as the FeO bearing molten slag is reduced by solid-carbon [17-18].

$$(FeO)_{(1)} + (C)_{(s)} = [Fe]_{(1)} + CO$$
$$\Delta G_1^\Theta = 113400 - 127.6T \text{ J/mol} \tag{12}$$

$$(FeO)_{(1)} + CO = [Fe]_{(1)} + CO_2$$
$$\Delta G_2^\Theta = 49390 + 40.2T \text{ J/mol} \tag{13}$$

$$C_{(s)} + CO^2 = 2CO$$
$$\Delta G_3^\Theta = 162790 - 167.8T \text{ J/mol} \tag{14}$$

Because of the existence of gas film, only Eqs. 13 and 14 can take place. The reduction kinetic model of FeO bearing molten slag using graphite crucible as reductant is shown in Fig. 7. The reduction of FeO in slag can be described as follow-
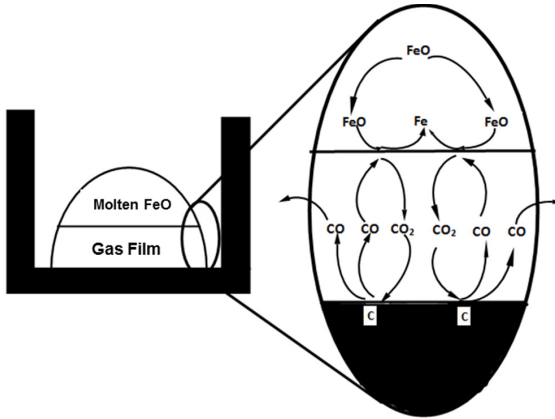
Fig. 7. Physical model of the reduction of FeO in molten slag by solid-carbon

ing steps: 1) FeO moves to slag-gas reaction interface. 2) FeO is reduced by CO, afterward produces CO_2; 3) CO_2 diffuses towards gas film-graphite interface; 4) Carbon gasifies into CO on gas film-graphite interface.

In this study, the gas resistance in mass transfer is ignored because of the low activation energies for gas diffusion [19]. Therefore, the reaction resistance mainly involves the carbon gasification reaction and the diffusion of FeO in the molten slag as listed in Eq. (15).

$$1/k = 1/k_c + 1/k_d \tag{15}$$

Where: $1/k$ is the total reaction resistance, $1/k_c$ is the resistance of carbon gasification, $1/k_d$ is the diffusion resistance of FeO. The proportions of carbon gasification resistance (f_1) and diffusion resistance of FeO (f_2) can be given as Eqs. (16 and 17).

$$f_1 = \frac{k_d}{k_d + k_c} \tag{16}$$

$$f_2 = \frac{k_c}{k_c + k_d} \tag{17}$$

Where: k can be obtained in the experiments. And k_c can be calculated by following method:

The carbon gasification rate can be proposed by Eq.18 based on a previous literature [20].

$$Q_C = z_c \frac{P_{CO_2}}{RT} \exp\left(-\frac{\Delta E}{RT}\right) \tag{18}$$

Where: Q_c is the carbon gasification rate (mol/cm²·min), P_{CO2} is partial pressure of CO_2, z_c is frequency factor, ΔE is activation energy for carbon gasification reaction. Because the reaction shown in Eq. (13) is in thermodynamic equilibrium, Eq. (19) can be therefore obtained according to Eq. (13).

$$K_2 = \frac{P_{CO_2}}{P_{CO}\gamma_{FeO}x_{FeO}} \tag{19}$$

Where: $P_{CO} + P_{CO2} = 1$, K_2 is the equilibrium constant for Eq. 13 (obtained from ΔG_2^Θ). P_{CO} is partial pressure of CO. γ_{FeO} is

activity coefficient of FeO in molten slag. x_{FeO} is mole fraction of FeO in slag. And Eq. 20 can be obtained by the simultaneous of Eqs. (18 and 19).

$$Q_C = \frac{z_c}{RT} \cdot \frac{K_2\gamma_{FeO}x_{FeO}}{1 + K_2\gamma_{FeO}x_{FeO}} \exp\left(-\frac{\Delta E}{RT}\right) \tag{20}$$

In present work, K_2 for Eq.13 is less than 0.30, and the mole fraction of FeO (x_{FeO}) in slag less than 0.13. Therefore, Eq.20 can be approximately expressed in the form of Eq. (21).

$$Q_C = \frac{Z}{RT} K_2\gamma_{FeO} \exp\left(-\frac{\Delta E}{RT}\right) * C_{FeO} \tag{21}$$

Where; $Z = z_c \times$ conversion factors of unit.

It is known that reduction rate is proportional to the FeO activity in slag. In the present work, assuming changes of the FeO activity coefficient (g_{FeO}) in slag are ignorable, the reaction rate is proportional to C_{FeO}. And k_c can be obtained as Eq. (22).

$$k_c = \frac{Z}{RT} K_2\gamma_{FeO} \exp\left(-\frac{\Delta E}{RT}\right) \tag{22}$$

The activation energy (ΔE) for carbon gasification reaction is 217.6 kJ/mol and frequency factor (z_c) is 1.5×10^{10} cm/min based on a previous literature [20,21].
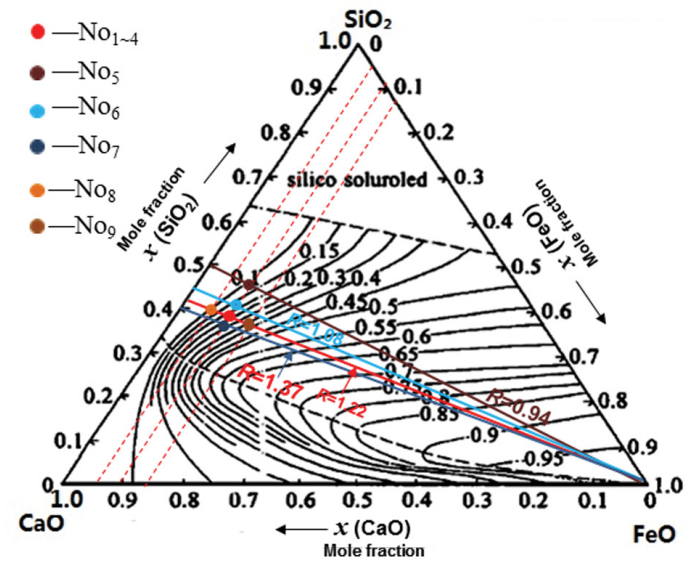

Fig. 8. Activity of FeO in CaO-MgO-FeO-SiO₂ system at 1773K

And the activity coefficient of FeO in slag (g_{FeO}) is obtained by interpolation method from the iso-activity diagram [22] shown in Fig. 8.

The relation between carbon gasification rate (Q_c) and concentration of FeO (C_{FeO}) can be obtained, so are the values of k_c based on Eq.(22) and k_d based on Eq.(15). The details are listed in Table 3.

From Table 3, one can conclude that the reduction process is controlled by both FeO diffusion and carbon gasification reaction in molten slag. However, the resistance of FeO diffusion is larger

TABLE 3

Comparison among $k \square k_c$ and k_d of the reduction of FeO in molten slag by graphite carbon

No$_i$ ($i = 1\sim9$)	T/K	R	x_{FeO}	γ_{FeO}	$k_c \times 100$	$k_d \times 100$	$k \times 100$	f_1	f_2
1	1773	1.22	0.084	3.01	177.62	12.46	11.27	6.56	93.44
2	1673	1.22	0.084	3.01	101.95	2.91	2.83	2.85	97.15
3	1723	1.22	0.084	3.01	131.79	6.96	6.61	5.02	94.98
4	1823	1.22	0.084	3.01	237.30	21.64	19.83	8.32	91.68
5	1773	0.94	0.084	1.57	92.64	8.72	7.97	8.60	91.40
6	1773	1.08	0.084	2.41	142.21	10.01	9.44	6.58	93.42
7	1773	1.37	0.084	2.98	175.84	13.89	12.87	7.32	92.68
8	1773	1.22	0.042	3.04	179.39	7.70	7.38	4.12	95.88
9	1773	1.22	0.126	3.19	188.24	18.07	16.49	8.76	91.24

than that of carbon gasification in molten slag, which indicates that the main restrictive step is the FeO diffusion in molten slag.
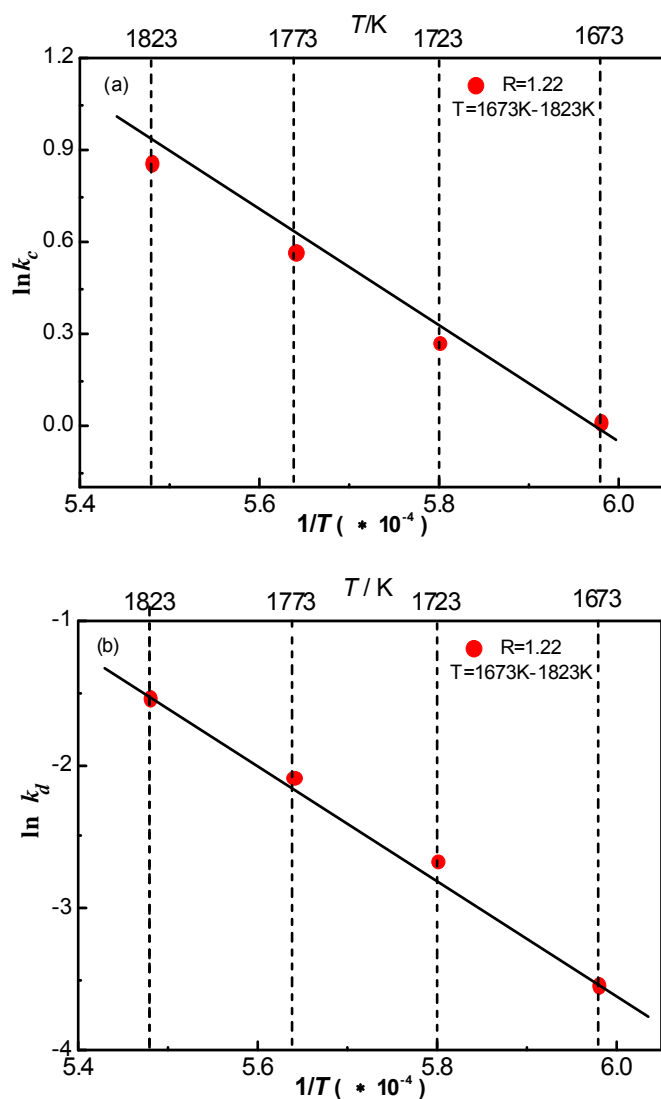
based on the curves of $\ln k_c - 1/T$ and $\ln k_d - 1/T$ in Fig. 9. The expressions of $\ln k_c - 1/T$ and $\ln k_d - 1/T$ are listed in forms of Eqs. (24 and 25), respectively.

$$\ln k_c = 10.95 - \frac{152977}{RT} \qquad (24)$$

$$\ln k_d = 21.95 - \frac{355007}{RT} \qquad (25)$$

The apparent activation energy for carbon gasification reaction in molten slag is 152.98 kJ/mol and the activation energy for the diffusion of FeO in molten slag is 355.01 kJ/mol, which means that the mass transfer of FeO in molten slag is more easily influenced by the temperature than that of carbon gasification reaction.

4. Conclusions

The reduction kinetics of FeO bearing molten slag (primary slag of BF) reduced by solid-carbon was investigated. The main findings could be summarized as follows.

1) The reduction reaction of FeO-CaO-SiO$_2$-Al$_2$O$_3$-MgO BF primary slag is a second-order reaction and the apparent activation energy of reduction of FeO in experimental slag system is 342.37 kJ/mol. Besides, the activation energy of the FeO diffusion of in molten slag is 355.01 kJ/mol, and activation energy of carbon gasification in molten slag is 152.98 kJ/mol.

2) The reduction rate of FeO is influenced by following factors, e.g. the experimental temperature (T), mass fraction of FeO ($w_{(FeO)}$), and basicity (R) of the slag. And the reduction rate is increasing higher as the T (increasing from 1673K to 1823K), $w_{(FeO)}$ (increasing from 5% to 15%) and R (increasing from 0.94 to 1.37) increases, respectively.

3) The reduction rate of the slag system considered here ($R = 1.22$, FeO-CaO-SiO$_2$-MgO-Al$_2$O$_3$) was obtained, which has been also verified by a series of experiments. The results have shown that this model can well describe the reduction of BF primary slag.

(a) $\ln k_c - 1/T$; (b) $\ln k_d - 1/T$
Fig. 9. Relationship of $\ln k_c - 1/T$ and $\ln k_d - 1/T$

Meanwhile, the activation energies for both carbon gasification reaction and FeO diffusion in molten slag can be calculated

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