Activity of MgO in CaO–SiO₂–MgO–Al₂O₃ Melts for Blast Furnace Slag at 1 873 K

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In this paper, slag-metal equilibrium experiments have been carried out for the determination of activity of MgO in CaO–SiO₂–MgO–Al₂O₃ melts for blast furnace slag at T=1 873 K using Sn as metal solvent and CaF₂–MgO slag as reference slag. Based on the obtained experimental results, the iso-activity contour for CaO–SiO₂–MgO–Al₂O₃ system was plotted. The effects of $R(w(\text{CaO})/w(\text{SiO}_2))$ and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on the activity of MgO was also discussed. The effects of R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on slag structure were analyzed by Fourier transform infrared spectroscopy (FT-IR). The results show that when $w(\text{Al}_2\text{O}_3)=20\%$ and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)=0.50$, the activity of MgO increased with the increase of R . When $w(\text{Al}_2\text{O}_3)=20\%$ and $R=1.30$, the activity of MgO increased with the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$. Through the analysis of FT-IR, the amount of free oxygen ions (O^{2-}) increases with the increase of R or $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ in slag, and these free oxygen ions interact with the bridge oxygen (O^0) of silicate, resulting in the gradual depolymerization of complex Si–O structure in slag.

KEY WORDS: blast furnace (BF); CaO–SiO₂–MgO–Al₂O₃ system; activity of MgO; reference slag method; iso-activity contours; FT-IR.

1. Introduction

Thermodynamic properties of the CaO–SiO₂–MgO–Al₂O₃ slag are of great importance.^{1–3)} With the consumption of high-quality iron ore resources, the grade of iron ore raw materials available to iron and steel enterprises is gradually decreasing. The use of high alumina iron ore makes the Al₂O₃ content in blast furnace slag high, which leads to the increase of slag viscosity, poor fluidity and reduction of desulphurization ability.^{4–6)} The activity of each component involved in the desulfurization reaction is an important factor affecting the desulfurization process. However, research on the component activity of high Al₂O₃ blast furnace slag produced by low-grade iron ore is really limited. Therefore, the experimental determination of the activity of high Al₂O₃ type CaO–SiO₂–MgO–Al₂O₃ quaternary blast furnace slag system components is of great significance for further research on the desulfurization ability of blast furnace slag and enriching the activity database.

Many researchers have tried to measure the activities in silicate melts. Su *et al.* measured the activity of MgO in the MgO–B₂O₃–SiO₂ slags at 1 723 K by slag-metal equilibrium technique.⁷⁾ The activity of MgO in the MgO–B₂O₃ binary system at T=1 723 K were measured with slag-metal equilibrium method by Wang and Huang *et al.*^{8,9)} The activity

of MgO in the MgO–B₂O₃ binary system at T=1 773 K and 1 823 K were measured by Zhang *et al.*, using slag-metal equilibration method. Sn was used as metal solvent, and B₂O₃–MgO slag was used as reference slag in their research.¹⁰⁾ Kume *et al.* experimentally determined the activity of MgO in the CaO–SiO₂–MgO and CaO–SiO₂–AlO_{1.5}–MgO systems at 1 823 and 1 873 K by equilibration the slag with Si based alloys.¹¹⁾ The activity of MgO in the MgO–CaF₂, MgO–CaF₂–Al₂O₃ and CaO–CaF₂–MgO–Al₂O₃ system at T=1 923 K were measured by Chen *et al.*, using slag-metal equilibration method, Sn was used as metal solvent, and MgO–CaF₂ slag was used as reference slag in their research.¹²⁾ Kambayashi *et al.* reported the activities of MgO in the MgO–SiO₂ system at 1 823 K.¹³⁾ There have been many studies on the activity determination of MgO in silicate melts, but there are few reports on the activity determination of MgO in CaO–SiO₂–MgO–Al₂O₃ quaternary slag system for high alumina blast furnace slag system. There are few reports on the use of FT-IR to explain the reaction mechanism of high Al₂O₃ blast furnace slag. Slag metal equilibrium method is a simple method to determine the activity of silicate system components. Its biggest advantage is that it does not rely on thermodynamic data and has high accuracy.

The slag-metal equilibrium study is a convenient method to measure activities in the CaO–SiO₂–MgO–Al₂O₃ system. In the present work, the MgO activities of silicate systems

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were experimentally determined at 1 873 K by slag-metal equilibration method, using Sn as metal solvent, $\text{CaF}_2\text{-MgO}$ slag as reference slag, focusing on the high Al_2O_3 concentration of BF slags. Based on the results of the measurement, the effects of R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on activity of MgO were discussed. The iso-activity contours for $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ system were plotted. The influence of different R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on slag structure was analyzed by FT-IR. Further study on the microstructure of blast furnace slag can better understand the relationship between chemical composition and metallurgical properties of slag, and provide a theoretical basis for determining reasonable slag making system. It is also of great significance to further study the desulfurization ability and rich activity database of blast furnace slag. The results of the present experimental work can be applied to improve the metallurgical properties of blast furnace slag.

2. Experimental

2.1. Principle of the Activity Determination

The principle equilibrium reactions between reference slag or measured slag and Mg in the molten Sn are represented by the following equations:

$$K_2 = \frac{a_{[\text{Mg}]} \cdot p_{\text{CO}}}{a_{(\text{MgO})} \cdot a_{\text{C}} \cdot p^\theta} \quad \text{..... (2)}$$

$$K_4 = \frac{a_{\text{ref}[\text{Mg}]} \cdot p_{\text{CO}}}{a_{\text{ref}(\text{MgO})} \cdot a_{\text{C}} \cdot p^\theta} \quad \text{..... (4)}$$

Where $a_{(\text{MgO})}$ and $a_{\text{ref}(\text{MgO})}$ are the MgO activities of the measured slag and reference slag relative to pure solid, respectively. $a_{[\text{Mg}]}$ and $a_{\text{ref}[\text{Mg}]}$ are the activities of Mg in molten Sn at equilibrium with the measured slag and the reference slag relative to infinite dilute solution, respectively. $p_{(\text{CO})}$ and p_{CO}^θ are the pressures of CO and standard atmosphere ($p_{(\text{CO})} = p_{\text{CO}}^\theta = 101\,325\text{ Pa}$), respectively. where a_{C} is the activity of carbon relative to pure solid. When reaction (1) and reaction (3) are at the same conditions, the equation $K_2 = K_4$ can be written as follows:

$$a_{(\text{MgO})} = a_{\text{ref}(\text{MgO})} \cdot \frac{a_{[\text{Mg}]}}{a_{\text{ref}[\text{Mg}]}} \quad \text{..... (5)}$$

Concentration of Mg in Sn is small enough to make the Henry's law suitable,^{10,12)} so $f_{[\text{Mg}]} = 1$. **Figure 1** is the phase diagram of $\text{CaF}_2\text{-MgO}$ binary slag system. When the mass fraction of MgO is more than 48 at 1 873 K, it is the saturated region of MgO. Therefore, the composition of point S($w(\text{CaF}_2)=45\%$ and $w(\text{MgO})=55\%$) was chosen as the reference slag in this study, and the activity of MgO is 1. In order to further determine the composition of S-point slag system at equilibrium in $\text{CaF}_2\text{-MgO}$ binary phase diagram, the composition of S-point oil cooled slag sample was analyzed by X-ray diffractometer, and the results are shown in **Fig. 2**. It can be seen from Fig. 2 that only CaF_2 and

Fig. 1. $\text{CaF}_2\text{-MgO}$ binary phase diagram and activity of MgO in the binary slag $\text{CaF}_2\text{-MgO}$.¹⁴⁾ (Online version in color.)

Fig. 2. S-point XRD analysis results of $\text{CaF}_2\text{-MgO}$ reference slag. (Online version in color.)

MgO are contained in the slag at equilibrium, which further proves that MgO at S point is in saturated state. Under the condition of 1 873 K, Chen *et al.*¹²⁾ tested the activity of MgO at point P($w(\text{CaF}_2)=45\%$ and $w(\text{MgO})=55\%$) of $\text{CaF}_2\text{-MgO}$ slag system, and the activity of MgO was 1. Thus, Eq. (5) can be simply derived from Eq. (6):

$$a_{(\text{MgO})} = \frac{x_{[\text{Mg}]}}{x_{\text{ref}[\text{Mg}]}} \quad \text{..... (6)}$$

Therefore, $a_{(\text{MgO})}$ can be calculated when $x_{(\text{Mg})}$ and $x_{\text{ref}[\text{Mg}]}$ were obtained from the experiments. where $x_{(\text{Mg})}$ and $x_{\text{ref}[\text{Mg}]}$ denote the concentration of Mg in Sn at equilibrium with the measured slag and the reference slag, respectively.

2.2. Experimental Procedure

In order to measure the activity of MgO in the silicate melt, solvent metal (Sn $\geq 99.9\%$) and the slag (measure slag or reference slag) were equilibrated in a MoSi_2 resistance furnace. The schematic diagram of experimental set up

is shown in **Fig. 3**. The temperature was controlled by a proportional-integral-differential (PID) controller which maintained it within ± 2 K. The experimental materials used high-purity CaO , SiO_2 , MgO and Al_2O_3 chemical reagents, metal Sn particles, CO gas and oil. The chemical reagents of CaO , SiO_2 , MgO and Al_2O_3 were dried at 105°C for 12–13 h. The slag to be tested is selected from the range of blast furnace slag composition, and the composition is shown in **Table 1**. According to the mass percentage, the dried CaO , SiO_2 , MgO and Al_2O_3 high-purity chemical reagents are weighed and loaded into the graphite crucible. When the furnace temperature of the muffle furnace rises to $1\,250^\circ\text{C}$, the graphite crucible containing high-purity chemical reagents is put into the muffle furnace for pre-melting treatment, and finally cooled and crushed to make a standby pre-melted slag. A six hole graphite crucibles was used in the experiment. About 5 g of solvent metal ($\text{Sn} \geq 99.9\%$) and 10 g of the slag (measure slag or reference slag) were filled in a graphite crucible. When the temperature of a tubular furnace sample rises to $700\text{--}800^\circ\text{C}$, CO is introduced, and the CO flow rate is controlled within $0.98\text{--}1.0$ L/min. The graphite crucible with the sample was inserted into the constant temperature zone of the furnace. When the temperature of a tube furnace sample rises to $1\,873$ K, the time will be started. After the balance time is reached, the graphite crucible shall be taken out and oil cooled by using a graphite rod. Thereafter, the metal and the slag were carefully separated for chemical analyses by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The changes in the chemical composition of the blast furnace slag in the experiment are shown in **Table 2**. From this table, it can be seen that the chemical composition of blast furnace slag is basically unchanged before and after the experiment, and the relative change rate is within 7%. Therefore, this paper discusses the influence of $R(w(\text{CaO})/w(\text{SiO}_2))$ and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on the activity of MgO based on the composition of the blast furnace slag before the experiment.

2.3. Equilibration Time

Due to the uncertainty of the equilibrium time required for the reaction, in order to ensure the equilibrium of the reaction in the experimental process and the accuracy of the experimental results, the equilibrium time should be explored under the condition that other test conditions

Table 1. Chemical compositions of measured slag.

No.	Slag compositions				R , -	$w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, -
	CaO	SiO_2	MgO	Al_2O_3		
1	35.85	34.14	10.0	20	1.05	0.50
2	37.51	32.49	10.0	20	1.15	0.50
3	38.89	31.11	10.0	20	1.25	0.50
4	40.21	29.78	10.0	20	1.35	0.50
5	42.39	32.60	5.0	20	1.30	0.25
6	41.26	31.73	7.0	20	1.30	0.35
7	40.13	30.86	9.0	20	1.30	0.45
8	39.00	30.00	11.0	20	1.30	0.55

Table 2. Change of slag composition during the experiment.

No.	Slag composition before experiment (mass%)				Slag composition after experiment (mass%)			
	CaO	SiO_2	MgO	Al_2O_3	CaO	SiO_2	MgO	Al_2O_3
1	35.85	34.14	10.0	20	35.41	33.35	9.26	19.39
2	37.51	32.49	10.0	20	36.62	32.02	9.46	19.75
3	38.89	31.11	10.0	20	38.33	30.84	9.51	19.63
4	40.21	29.78	10.0	20	39.32	29.27	9.77	19.72
5	42.39	32.60	5.0	20	41.87	31.85	4.63	19.35
6	41.26	31.73	7.0	20	40.64	30.98	6.54	19.31
7	40.13	30.86	9.0	20	39.22	29.78	8.30	19.56
8	39.00	30.00	11.0	20	38.58	29.83	10.22	19.61

Fig. 3. Schematic of experimental apparatus: 1-gas outlet (CO); 2-water intake; 3-heating unit of MoSi_2 ; 4- Al_2O_3 tube; 5-graphite crucible; 6-gas inlet (CO); 7-carbonic oxide (CO); 8-water outlet; 9-30%Rh/Pt-60%Rh; 10-30%Rh/Pt-60%Rh; 11-reference slag: $\text{CaF}_2\text{--MgO}$; 12-solvent metal ($\text{Sn} \geq 99.99\%$); 13-measured slag: $\text{CaO--SiO}_2\text{--MgO--Al}_2\text{O}_3$; 14-solvent metal ($\text{Sn} \geq 99.99\%$); 15-temperature control system; 16-computer.

Fig. 4. Mg content in metallic Sn under different reaction time.

are exactly the same. The content of slag composition of equilibrium experiment is as follows: $w(\text{CaO})=47.02\%$, $w(\text{SiO}_2)=36.17\%$, $w(\text{MgO})=4.8\%$ and $w(\text{Al}_2\text{O}_3)=12\%$. The equilibrium time was set at 6, 12, 18 and 26 h, respectively. The relationship between Mg content in molten Sn and time was shown in Fig. 4. It can be seen from Fig. 4 that the content of Mg in Sn hardly change after 18 h of reaction, so it can be considered that the reaction has basically reached equilibrium. Therefore, the equilibrium time was determined to be 24 h.

3. Results and Discussion

Although many researchers have studied the activity of slag components, the influence of slag composition on the activity is discussed. It is rare to explain the reaction mechanism of high alumina blast furnace slag from the slag structure. Based on the experimental data, the effects of R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on the activity of MgO were discussed. FT-IR was used to analyze the effect of different R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on the slag structure. The in-depth study on the microstructure of blast furnace slag is of great significance to further study the desulfurization ability of blast furnace slag. For the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ quaternary slag system, a variety of complex compounds are formed at high temperature, and the main reaction formula is shown in Table 3. The oxygen ions in silicate melt can be divided into three types: bridged oxygen (O^0), non bridged oxygen (O^-) and free oxygen (O^{2-}).^{17,18} The silicate melt is tetrahedral structure, and the bridging oxygen (O^0) and non bridging oxygen (O^-) connects different tetrahedrons together to form a three-dimensional continuous space network structure. Basic oxides can break the three-dimensional network structure by releasing free oxygen ions and bridging oxygen to form non bridging oxygen. The amount of three kinds of oxygen in slag changes with the change of slag chemical composition, and the network structure will also change accordingly. Therefore, the change of slag structure can also be expressed by the amount of bridged oxygen (O^0), non bridged oxygen (O^-) and free oxygen (O^{2-}). The results show that the wave number of FT-IR analysis of silicate slag

Table 3. Main reaction equations of $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ quaternary blast furnace slag system.

Equations	$\Delta G^\theta/(\text{J}\cdot\text{mol}^{-1})^{15,16}$	No.
$(\text{Ca}^{2+}+\text{O}^{2-})+\text{SiO}_2=\text{CaSiO}_3$	$-92\,500-2.57T$	(7)
$2(\text{Ca}^{2+}+\text{O}^{2-})+\text{SiO}_2=\text{Ca}_2\text{SiO}_4$	$-118\,800-11.3T$	(8)
$3(\text{Ca}^{2+}+\text{O}^{2-})+\text{SiO}_2=\text{Ca}_3\text{SiO}_5$	$-118\,800-6.77T$	(9)
$(\text{Ca}^{2+}+\text{O}^{2-})+\text{Al}_2\text{O}_3=\text{CaO}\cdot\text{Al}_2\text{O}_3$	$-18\,000-18.83T$	(10)
$(\text{Ca}^{2+}+\text{O}^{2-})+2\text{Al}_2\text{O}_3=\text{CaO}\cdot 2\text{Al}_2\text{O}_3$	$-86\,100-205.1T$	(11)
$3(\text{Ca}^{2+}+\text{O}^{2-})+\text{Al}_2\text{O}_3=3\text{CaO}\cdot\text{Al}_2\text{O}_3$	$-12\,600-24.69T$	(12)
$(\text{Mg}^{2+}+\text{O}^{2-})+\text{SiO}_2=\text{MgSiO}_3$	$-41\,100+6.17T$	(13)
$2(\text{Mg}^{2+}+\text{O}^{2-})+\text{SiO}_2=\text{Mg}_2\text{SiO}_4$	$-67\,200+4.31T$	(14)
$(\text{Mg}^{2+}+\text{O}^{2-})+\text{Al}_2\text{O}_3=\text{MgO}\cdot\text{Al}_2\text{O}_3$	$-35\,600-2.09T$	(15)

is generally concentrated in the region of $400\text{--}1\,200\text{ cm}^{-1}$, and the $[\text{SiO}_4]$ tetrahedron structure is characterized in the range of $800\text{--}1\,200\text{ cm}^{-1}$.^{19–22}

3.1. Iso-activity Contours of MgO in $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ Quaternary Slag System

Under the condition of $T = 1\,873\text{ K}$, the activity of MgO in $\text{CaO-SiO}_2\text{-MgO-}20\%\text{Al}_2\text{O}_3$ quaternary slag system was determined by slag metal equilibrium method with Sn as metal solvent and $\text{CaF}_2\text{-MgO}$ as reference slag. The experimental results are shown in Tables 4 and 5. It can be seen from Table 5 that when the reaction reaches equilibrium, the content of Mg in Sn is very low. According to the experimental results in Table 5, the iso-activity diagram of MgO in $\text{CaO-SiO}_2\text{-MgO-}20\%\text{Al}_2\text{O}_3$ quaternary slag system at $1\,873\text{ K}$ is drawn, as showed in Fig. 5. In order to further verify the accuracy of the iso-activity diagram of MgO in $\text{CaO-SiO}_2\text{-MgO-}20\%\text{Al}_2\text{O}_3$ quaternary slag system, which is drawn according to the experimental results in Table 5. The $H(w(\text{CaO})=40.69\%, w(\text{SiO}_2)=31.30\%, w(\text{MgO})=8.0\%, w(\text{Al}_2\text{O}_3)=20\%)$ point is selected on the line of MgO activity equal to 0.5 in Fig. 5, and the experiment is carried out under the same other experimental conditions, and the results are shown in Fig. 5. It can be seen from Fig. 5 that the activity of MgO at H point is 0.4928, and its activity value is on the line of MgO activity equal to 0.5, which demonstrates the accuracy of MgO iso-activity diagram of $\text{CaO-SiO}_2\text{-MgO-}20\%\text{Al}_2\text{O}_3$ quaternary slag system.

3.2. Effect of R on Activity of MgO

The effect of R on the activity of MgO in the slag is shown in Fig. 6. When $w(\text{MgO})/w(\text{Al}_2\text{O}_3)=0.50$, $w(\text{Al}_2\text{O}_3)=20\%$ and $R=1.05, 1.15, 1.25$ and 1.35 in slags, the activity of MgO increased with the increase of R . With the increase of R , the content of CaO increases, the content of SiO_2 decreases, and the content of MgO and Al_2O_3 remains unchanged. CaO and MgO are both alkaline oxides, which can dissociate free oxygen ions (O^{2-}) in slag. The ionic radius of Ca^{2+} is larger than that of Mg^{2+} , the bond energy between Ca^{2+} and free oxygen ion (O^{2-}) is smaller than that between Mg^{2+} and free oxygen ion (O^{2-}), and the free oxygen ion (O^{2-}) dissociated from CaO is dominant. With the increase of R , the concentration of CaO in slag increases continuously, which promotes the reaction (7)–(12) forward.

The free oxygen ions (O^{2-}) dissociated from CaO are enough to react with SiO_2 and Al_2O_3 in high temperature melt to form silicate ions and aluminate ions, which greatly consume acid oxides and increase the activity of MgO in slag. **Figure 7** shows the FT-IR of different R slag samples.

It can be found from the results of FT-IR in Fig. 7 that with the increase of R , the grooves of $[SiO_4]$ tetrahedral structure at the wavenumber of $800\text{--}1\,200\text{ cm}^{-1}$ gradually become shallow and flat, which indicates that the complex silicate structure polymerized in the form of SiO_2 decreases. With the increase of R , the content of CaO increases, and the dissociated free oxygen ion (O^{2-}) increases. The dissociated free oxygen ion (O^{2-}) is enough to interact with the bridging oxygen (O^0) of silicate, so that the complex Si–O structure in slag is gradually depolymerized, and the activity of MgO in slag is continuously increased. Park J H²³⁾ study found that with the increase of R , the degree of polymerization of slag decreased gradually. In the molten state, CaO

decomposed into O^{2-} and Ca^{2+} , which could depolymerize the complex Si–O structure in slag gradually, thus reducing the degree of polymerization of slag, which was consistent with the experimental results.

Table 4. Concentrations of Mg in Sn for three groups after equilibrium and the activities of MgO in CaF_2 –MgO system.

Reference slag	$x_{ref}[Mg]$, -			Average value	$a_{ref}(MgO)$, -
	1	2	3		
CaF_2 –MgO	0.00301	0.00302	0.00303	0.00302	1

Fig. 6. The effect of R on the activity of MgO in the CaO – SiO_2 – MgO – Al_2O_3 system at 1 873 K.

Table 5. Slag compositions, the contents of elements in Sn and the activities of MgO after equilibrium in CaO – SiO_2 – Al_2O_3 – MgO system at 1 873 K.

No.	Slag compositions (mass%)				$x_{[Al]}$, -	$x_{[Si]}$, -	$x_{[Ca]}$, -	$x_{[Mg]}$, -	$a(MgO)$, -
	CaO	SiO_2	MgO	Al_2O_3					
1	35.41	33.35	9.26	19.39	0.000264	0.000380	0.001921	0.001355	0.4478
2	36.62	32.02	9.46	19.75	0.000220	0.000253	0.002157	0.001550	0.5121
3	38.33	30.84	9.51	19.63	0.000176	0.000169	0.002835	0.001628	0.5379
4	39.32	29.27	9.77	19.72	0.000176	0.000084	0.003631	0.001929	0.6376
5	41.87	31.85	4.63	19.35	0.000220	0.000295	0.004014	0.001282	0.4236
6	40.64	30.98	6.54	19.31	0.000220	0.000211	0.003572	0.001438	0.4751
7	39.22	29.78	8.30	19.56	0.000220	0.000127	0.003484	0.001730	0.5716
8	38.58	29.83	10.22	19.61	0.000220	0.000084	0.003690	0.001959	0.6472

Fig. 5. Iso-activity contours for MgO in the CaO – SiO_2 – MgO – $20\%Al_2O_3$ system at 1 873 K. (Online version in color.)

Fig. 7. The FT-IR results of different R slag samples at 1873 K. (Online version in color.)

3.3. Effect of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on Activity of MgO

The effect of R on the activity of MgO in the slag is given in Fig. 8. When $R=1.30$, $w(\text{Al}_2\text{O}_3)=20\%$ and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)=0.25, 0.35, 0.45$ and 0.55 in slags, the activity of MgO increased with the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$. With the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, the MgO concentration in the slag increases continuously, which promotes the forward reaction of (13)–(15). MgO provides more free oxygen ions (O^{2-}) and reacts with SiO_2 and Al_2O_3 in high temperature melt to form silicate and aluminate ions, which greatly consumes acid oxides and leads to the decrease of MgO activity in slag. But with the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, the content of MgO in the slag increases, and the activity of MgO in the slag keeps increasing. Figure 9 shows the FT-IR of different $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ slag samples. It can be found from the results of FT-IR in Fig. 9 that with the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, the grooves of $[\text{SiO}_4]$ tetrahedral structure at the wavenumber of $800\text{--}1200\text{ cm}^{-1}$ gradually become shallow and flat, which indicates that the complex silicate structure polymerized in the form of SiO_2 decreases. With the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, the MgO content in the slag increases, and the free oxygen ions (O^{2-}) dissociated from the slag increase. The interaction between free oxygen ion (O^{2-}) and bridging oxygen (O^0) of silicate leads to the depolymerization of complex Si–O structure in slag and the decrease of MgO activity in slag. But with the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, the content of MgO in the slag increases, and the activity of MgO in the slag keeps increasing. Hao J L²⁴⁾ studied the effect of

Fig. 8. The effect of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on the activity of MgO in the CaO– SiO_2 –MgO– Al_2O_3 system at 1873 K.

Fig. 9. The FT-IR results of different $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ slag samples at 1873 K. (Online version in color.)

$w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on slag structure by FT-IR. It is found that the combination of free oxygen ions (O^{2-}) in slag and bridging oxygen (O^0) in silicate destroys the Si–O structure and depolymerizes the complex Si–O structure into simple units, which is consistent with the experimental results.

Table 6. The activity coefficient of Mg in Sn at 1 873 K.

$x_{[\text{Mg}]}$, -	0.001355	0.00155	0.001628	0.001929	0.001282	0.001438	0.00173	0.001959
$a_{[\text{Mg}](\text{R})}$, -	0.004297	0.004914	0.005162	0.006118	0.004065	0.004559	0.005485	0.006211
$\gamma_{[\text{Mg}]}$	3.1713	3.1704	3.1706	3.1718	3.1707	3.1704	3.1706	3.1703

3.4. Thermodynamics of Magnesium in Molten Tin

According to the present results, the activity coefficient of Mg in Sn at Raoultian standard state can be obtained.

$$K^\theta = \frac{a_{[\text{Mg}]} \cdot p_{\text{CO}}}{a_{(\text{MgO})} \cdot a_{\text{C}} \cdot p^\theta} \dots (17)$$

$$\Delta G^\theta = 615\,200 - 289.82T \text{ (J/mol)}^{(25)} \dots (18)$$

Where $a_{(\text{MgO})}$ is the MgO activity of the measured slag relative to pure solid. $a_{[\text{Mg}]}$ is the activity of Mg in molten Sn at equilibrium with the measured slag relative to infinite dilute solution. p_{CO} and p_{CO}^θ are the pressures of CO and standard atmosphere ($p_{\text{CO}} = p_{\text{CO}}^\theta = 101\,325 \text{ Pa}$), respectively. a_{C} , activity of carbon, is 1 when pure substance standard is taken as pure substance standard state. Thus, Eq. (17) can be simply derived from Eq. (19):

$$K^\theta = \frac{a_{[\text{Mg}]}}{a_{(\text{MgO})}} \dots (19)$$

According to Eq. (18), $\lg K^\theta$ can be obtained as Eq. (20):

$$\lg K^\theta = -\frac{615\,200}{19.147 \cdot 1873} + \frac{289.82}{19.147} = -2.018 \dots (20)$$

$$K^\theta = 0.009596 \dots (21)$$

The activity of magnesium can be calculated by as follows:

$$a_{[\text{Mg}]} = K^\theta \cdot a_{(\text{MgO})} \dots (22)$$

According to Eq. (22), the activity coefficient of Mg in Sn at 1 873 K is calculated, and the results are shown in **Table 6**. According to formula (19), when the temperature is 1 873 K, the equilibrium constant (K^θ) is constant. The activity value of MgO in the same blast furnace slag systems is equal, so the activity value of Mg in the metal Sn is a fixed value.

4. Conclusion

The activity of MgO in $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ quaternary slag system was determined by reference slag method with Sn as metal solvent and $\text{CaF}_2\text{-MgO}$ as reference slag at 1 873 K. Based on the experimental data, the effects of R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on the activity of MgO were discussed.

The activity diagram of MgO in $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ quaternary slag system was drawn. The influence of different R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$ on slag structure was analyzed by FT-IR. The conclusions are as follows: 1) When $w(\text{Al}_2\text{O}_3)=20\%$ and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)=0.50$, the

activity of MgO increased with the increase of R . 2) When $w(\text{Al}_2\text{O}_3)=20\%$ and $R=1.30$, the activity of MgO increased with the increase of $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$. 3) It is confirmed by FT-IR that with the increase of R and $w(\text{MgO})/w(\text{Al}_2\text{O}_3)$, the dissociated free oxygen ions (O^{2-}) in the slag increased. The dissociated free oxygen ions (O^{2-}) interacted with the bridging oxygen (O^0) of silicate, resulting in the dissociation of complex Si-O structure into simple units, and the activity of MgO increased.

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REFERENCES

- 1) X. Yuan, J. L. Zhang, R. Mao and Z. J. Liu: *J. Northeast. Univ. (Nat. Sci.)*, **36** (2015), 1609.
- 2) K. Morita, K. Kume and N. Sano: *ISIJ Int.*, **40** (2000), 554.
- 3) R. H. Rein and J. Chipman: *Trans. Metall. Soc. AIME*, **233** (1965), 415.
- 4) H. S. Han, F. M. Shen, X. Jiang, C. G. Bi, H. Y. Zheng and Q. J. Gao: *J. Iron Steel Res. Int.*, **26** (2019), 1171.
- 5) J. H. Park, D. J. Min and H. S. Song: *Metall. Mater. Trans. B*, **35** (2004), 269.
- 6) N. Saito, N. Hori, K. Nakashima and K. Mori: *Metall. Mater. Trans. B*, **34** (2003), 509.
- 7) Y. Su, S. X. Tong and Z. C. Wang: *J. Chem. Thermodyn.*, **28** (1996), 1103.
- 8) Z. C. Wang, S. X. Tong, X. Liu, Y. Su and F. Cao: *J. Chem. Thermodyn.*, **27** (1995), 873.
- 9) X. M. Huang, T. Fujisawa and C. Yamauchi: *ISIJ Int.*, **36** (1996), 133.
- 10) C. J. Zhang and C. L. Ji: *Acta Metall. Sin.*, **4** (1989), 240.
- 11) K. Kume, K. Morita, T. Miki and N. Sano: *ISIJ Int.*, **40** (2000), 561.
- 12) C. X. Chen and W. X. Zhao: *Acta Metall. Sin.*, **19** (1983), 1.
- 13) S. Kambayashi and E. Kato: *J. Chem. Thermodyn.*, **15** (1983), 701.
- 14) M. Allibert: *Slag Atlas*, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 188.
- 15) J. Zhang: *Computational Thermodynamics of Metallurgical Melts and Solutions*, Metallurgical Industry Press, Beijing, (2007), 245.
- 16) E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, (1980), 8.
- 17) C. Fincham and F. D. Richardson: *Proc. R. Soc. Lond. A*, **223** (1954), 40.
- 18) K. C. Mills: *ISIJ Int.*, **33** (1993), 148.
- 19) H. Kim, W. H. Kim, I. Sohn and D. J. Min: *Steel Res. Int.*, **81** (2010), 261.
- 20) S. M. Han, J. G. Park and I. Sohn: *J. Non-Cryst. Solids*, **357** (2011), 2868.
- 21) K. X. Jiao, J. L. Zhang, Z. Y. Wang, C. L. Chen and Y. X. Liu: *Steel Res. Int.*, **88** (2017), 1600296.
- 22) Y. Sun, H. Wang and Z. Zhang: *Metall. Mater. Trans. B*, **49** (2018), 677.
- 23) J. H. Park, D. J. Min and H. S. Song: *ISIJ Int.*, **42** (2002), 344.
- 24) J. L. Hao: Master thesis, Chongqing University, (2014), <https://kns.cnki.net/kcms/detail/detail.aspx?dbcode=CMFD&dbname=CMFD201501&filename=1014044754.nh&uniplatform=NZKPT&v=maMkEDQFYxEKZFttIbyWQV%25mmd2FV5H7YLG5VAS4RQN4dGWQkO%25mmd2FgsFiB%25mmd2FtDvt4m%25mmd2BKUzQk>, (accessed 2014-05-01).
- 25) C. H. Dai and X. P. Zhang: *J. Northeast. Univ. (Nat. Sci.)*, **17** (1996), 381.