Phase Equilibria Studies in the CaO–SiO₂–Al₂O₃–MgO System with CaO/SiO₂ Ratio of 1.10

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Phase equilibria and liquidus temperatures in the CaO–SiO₂–Al₂O₃–MgO system with CaO/SiO₂ weight ratio of 1.10 have been experimentally determined by means of high temperature equilibration and quenching technique followed by electron probe X-ray microanalysis. Isotherms in the interval of 20 K between 1 613 and 1 733 K were determined in the primary phase fields of dicalcium silicate, wollastonite, merwinite, periclase, spinel and melilite that are relevant to ironmaking slags. Effects of Al₂O₃, MgO and CaO/SiO₂ ratio on the liquidus temperatures have been discussed to assist optimum operation of iron blast furnace. Compositions of the solid solutions corresponding to the liquidus have been accurately measured that will be used for development of the thermodynamic database.

KEY WORDS: phase equilibria; liquidus temperature; CaO–SiO₂–Al₂O₃–MgO system; blast furnace slags; EPMA.

1. Introduction

In modern blast furnace (BF) process, the new challenges such as low gas permeability and formation of hearth accretion will constantly arise with the increasing use of low grade iron ores and poor fuels.^{1–3)} It is essential to optimise the BF slag system for smooth operation and low cost requirement. Therefore, accurate phase equilibria become more important to explain the effects of Al₂O₃ and MgO on operational temperature as the oxide system CaO–SiO₂–Al₂O₃–MgO forms a base for the tapping ironmaking slag. The phase diagrams in the system CaO–SiO₂–Al₂O₃–MgO have been summarised in Slag Atlas in the form of pseudo-ternary sections with the isotherms of 100 K interval at fixed concentrations of Al₂O₃ or MgO.⁴⁾ In the modern industry the operating parameters can be controlled more accurately. The larger intervals of compositions and temperatures in the previous phase diagrams cannot meet the requirements of current operations. Our recent work⁵⁾ showed the significant differences of the phase diagrams in the Al₂O₃–CaO–MgO–SiO₂ system from those reported in the early studies.^{6–8)} In addition, melilite solid solutions of Al₂O₃–CaO–MgO–SiO₂ system, in which industrial slags are operated, are important for optimisation of thermodynamic database. There are lack of melilite solid solution data reported previously. Hence, accurate phase equilibria data are of importance for both industrial and scientific interests.

The binary basicity (CaO/SiO₂ weight ratio) of BF slags

are mostly between 1.10 and 1.30 and it does not change significantly in a particular ironmaking plant. In modern ironmaking operations, the hot metal and slag temperatures need to be controlled within a narrow range to obtain stable BF operating condition. Phase equilibria and liquidus temperatures in the CaO–SiO₂–Al₂O₃–MgO system with CaO/SiO₂ weight ratio of 1.30 have been reported recently by the present authors.⁵⁾ The present study is focusing on the liquidus surfaces in the CaO–SiO₂–Al₂O₃–MgO system with CaO/SiO₂ of 1.10 to cover the composition range of iron BF final slags.

2. Experimental

The experimental procedure in this investigation has been described in details in a previous paper.⁵⁾ In brief, the experiments were carried out using a vertical electric resistance furnace. High-purity reagent powders of Al₂O₃, SiO₂, MgO and CaCO₃ were mixed and pelletized according to the required compositions, then placed in the hot zone of furnace to be premelted at a temperature 20–50 K higher than the desired temperature to ensure the homogeneous slag. The temperature was then decreased to the required one to achieve equilibration. Graphite crucible was used to hold the samples and ultrahigh purity Ar atmosphere was flashed continuously to protect the graphite crucibles. SiO gas may be generated by the reaction of graphite with SiO₂ in the slag. As a result, the initial bulk composition of the sample could change. However, the compositions of the liquid and solid phases of quenched sample were measured after the experiment. The change of slag bulk composition

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only affects the ratios of liquid to solid but does not change the phase compositions. A Pt-30 pct Rh/Pt-6 pct Rh thermocouple placed in an alumina sheath was located adjacent to the sample to monitor the temperature. The temperature of the furnace was controlled within 2 K and overall temperature uncertainty is within 5 K. The samples were directly quenched into water after the equilibration, then dried, mounted and polished for metallographic analysis. The microstructures were examined by scanning electron microscopy coupled with energy-dispersive spectroscopy analysis (SEM-EDS). Compositions of the liquid and solid phases were measured by a JEOL JXA-8200 Electron Probe X-Ray Microanalyser (EPMA) with Wavelength Dispersive Spectrometers (WDS). The EPMA measurement conditions were the same as previous work.⁵⁾ The homogeneity of the phase can be confirmed by the EPMA measurements in different areas of the quenched sample. Usually 8–20 points of liquid phase and 3–5 points of solid phase were measured

from different areas by EPMA. The sample with the standard deviation of the phase compositions less than 1% will be accepted and used to construct the phase diagram.

3. Results and Discussions

3.1. Description of the Pseudo-ternary Section

Over 150 experiments have been carried out in the CaO–SiO₂–Al₂O₃–MgO system with the CaO/SiO₂ weight ratio of 1.10. The composition range covers Al₂O₃ concentration up to 25 wt% and MgO up to 20 wt%. Dicalcium silicate, wollastonite, spinel, periclase, merwinite and melilite were found to be the primary phases in the composition range investigated. Typical microstructures observed in the quenched samples are presented in **Fig. 1**. Figure 1 shows the equilibrium of liquids with (a) merwinite, (b) dicalcium silicate (c) wollastonite, (d) melilite, (e) spinel and (f) merwinite and melilite respectively. CaO/SiO₂ ratio in

Fig. 1. Typical microstructures of slags quenched from (a) merwinite, (b) dicalcium silicate (c) wollastonite, (d) melilite and (e) spinel primary phase fields and (f) merwinite and melilite phase boundary.

dicalcium silicate, merwinite and melilite are mostly higher than 1.10. Precipitation of these solid phases from the melt will result in lower CaO/SiO₂ ratio in the liquid phase. The difficulty in controlling CaO/SiO₂ ratio at 1.10 can be overcome by preparing initial mixtures with slightly higher CaO/SiO₂ ratios. The compositions of liquid and solid phases measured by EPMA after the equilibration are presented in **Table 1**. EPMA measurements show that the compositions of dicalcium silicate (Ca₂SiO₄), wollastonite (CaSiO₃), spinel (MgO·Al₂O₃), and merwinite (3CaO·MgO·2SiO₂) are closed to their stoichiometry. Melilite is the solid solution between akermanite (2CaO·MgO·2SiO₂) and gehlenite (2CaO·Al₂O₃·SiO₂).

Table 1. Experimental results in the system CaO–SiO₂–Al₂O₃–MgO with CaO/SiO₂ ratio.

Experiment No.	Temperature (K)	Phases	Composition (wt%)				CaO/SiO ₂
			CaO	MgO	Al ₂ O ₃	SiO ₂	
Liquid							
148	1 633	Liquid	45.2	5.9	6.9	42.0	1.08
150	1 633	Liquid	44.8	6.0	9.0	40.2	1.11
179	1 653	Liquid	43.9	6.8	9.9	39.5	1.11
200	1 653	Liquid	48.5	2.6	5.6	43.3	1.12
141	1 673	Liquid	43.7	8.3	9.6	38.4	1.14
199	1 673	Liquid	48.2	5.2	3.7	43.0	1.12
154	1 693	Liquid	46.8	7.4	4.1	41.7	1.12
156	1 693	Liquid	43.7	9.0	9.2	38.1	1.15
158	1 693	Liquid	40.9	11.7	11.9	35.6	1.15
232	1 693	Liquid	38.9	10.8	14.5	35.9	1.08
227	1 713	Liquid	39.0	9.7	16.6	34.7	1.12
147	1 733	Liquid	45.2	9.3	3.7	41.7	1.08
149	1 733	Liquid	42.1	11.2	7.6	39.1	1.08
175	1 733	Liquid	47.2	9.4	2.0	41.3	1.14
233	1 733	Liquid	42.1	0.0	20.9	37.0	1.14
234	1 733	Liquid	40.9	4.9	17.3	36.9	1.11
Liquid with one oxide solid							
Melilite primary phase field							
174	1 613	Liquid	46.4	5.0	7.9	40.6	1.14
		Melilite	41.3	10.9	9.0	38.6	
180	1 613	Liquid	46.5	5.2	6.1	42.2	1.10
		Melilite	41.1	13.0	3.5	42.4	
198	1 613	Liquid	45.9	0.0	13.9	40.2	1.14
		Melilite	41.2	0.0	36.8	21.9	
196	1 613	Liquid	45.0	3.7	10.8	40.6	1.11
		Melilite	41.3	6.6	20.5	31.5	
144	1 633	Liquid	44.4	3.8	11.5	40.2	1.11
		Melilite	41.0	5.9	21.7	31.4	
146	1 633	Liquid	43.2	0.0	16.3	40.5	1.07
		Melilite	40.6	0.0	36.6	22.8	
155	1 633	Liquid	46.0	5.8	8.4	39.7	1.16
		Melilite	42.0	10.1	10.2	37.7	
Merwinite primary phase field							
157	1 633	Liquid	46.7	6.0	5.6	41.7	1.12
		Merwinite	52.1	12.0	0.1	35.9	
171	1 653	Liquid	44.8	7.4	7.9	39.8	1.13
		Merwinite	51.6	12.3	0.0	36.0	
140	1 673	Liquid	44.9	7.4	7.5	40.2	1.12

		Merwinite	51.8	12.1	0.1	36.0				Spinel	0.4	28.1	71.3	0.2
197	1 673	Liquid	46.4	7.2	4.5	41.9	1.11	3	1 733	Liquid	35.8	14.1	16.9	33.1 1.08
		Merwinite	51.8	12.2	0.0	35.9				Spinel	0.4	28.0	71.4	0.2
60	1 673	Liquid	37.9	14.2	13.1	34.7	1.09	5	1 733	Liquid	35.6	10.2	21.1	33.1 1.08
		Merwinite	51.1	12.6	0.1	36.1				Spinel	0.4	27.9	71.6	0.1
63	1 673	Liquid	39.0	12.5	12.4	36.0	1.08	Liquid with more oxide solids						
		Merwinite	51.3	12.1	0.1	36.5		211	1 593	Liquid	45.6	0.0	13.4	41.0 1.11
42	1 693	Liquid	37.9	14.2	12.3	35.5	1.07			Wollastonite	48.3	0.0	0.0	51.7
		Merwinite	50.6	12.8	0.1	36.4				Melilite	41.2	0.0	36.4	22.3
43	1 693	Liquid	40.1	11.0	10.4	38.3	1.05	152	1 633	Liquid	45.2	6.3	8.0	40.5 1.11
		Merwinite	50.9	12.7	0.1	36.3				Merwinite	51.8	11.9	0.1	36.2
56	1 693	Liquid	38.3	13.9	12.1	35.6	1.07			Melilite	41.6	11.8	6.2	40.4
		Merwinite	52.3	12.1	0.1	35.5		135	1 673	Liquid	37.6	14.2	14.0	34.2 1.10
173	1 693	Liquid	42.0	11.1	8.7	38.1	1.10			Spinel	0.1	28.0	71.7	0.1
		Merwinite	51.4	12.5	0.0	36.0				Merwinite	51.1	12.4	0.1	36.4
195	1 693	Liquid	46.2	8.7	2.5	42.6	1.08			Melilite	41.2	3.2	29.0	26.5
		Merwinite	51.7	12.3	0.0	36.0		246	1 673	Liquid	41.6	9.9	10.3	38.2 1.09
153	1 713	Liquid	43.1	10.8	7.8	38.3	1.13			Merwinite	50.9	12.5	0.1	36.6
		Merwinite	51.6	12.2	0.0	36.1				Melilite	41.0	9.2	14.1	35.8
151	1 733	Liquid	39.5	14.6	9.5	36.4	1.09	139	1 673	Liquid	46.6	6.6	3.7	43.1 1.08
		Merwinite	50.9	12.6	0.1	36.4				Ca ₂ SiO ₄	62.8	2.6	0.1	34.5
		Merwinite	52.3	12.1	0.1	35.5				Merwinite	52.0	11.8	0.0	36.2
<i>Ca₂SiO₄ primary phase field</i>								2	1 693	Liquid	36.8	15.8	13.3	34.1 1.08
214	1 633	Liquid	48.2	4.9	3.9	43.0	1.12			Spinel	0.6	27.8	71.0	0.4
		Ca ₂ SiO ₄	62.7	2.0	0.3	35.1				Merwinite	50.7	12.7	0.1	36.5
<i>Wollastonite primary phase field</i>								49	1 693	Liquid	36.5	16.5	13.3	33.6 1.09
209	1 613	Liquid	46.1	0.0	11.6	42.3	1.09			Spinel	0.1	28.5	71.3	0.1
		Wollastonite	48.1	0.0	0.0	51.9				Merwinite	50.9	12.6	0.1	36.5
210	1 613	Liquid	46.3	0.0	12.2	41.5	1.12	193	1 713	Liquid	46.7	9.1	2.2	42.1 1.11
		Wollastonite	48.3	0.0	0.1	51.6				Periclase	61.7	3.4	0.1	34.8
213	1 613	Liquid	45.3	2.7	9.1	42.8	1.06			Merwinite	51.9	12.3	0.0	35.8
		Wollastonite	48.3	0.0	0.1	51.6		44	1 733	Liquid	35.5	9.5	22.3	32.6 1.09
201	1 633	Liquid	49.1	0.0	8.8	42.1	1.17			Spinel	0.1	28.5	71.3	0.1
		Wollastonite	48.3	0.0	0.0	51.7				Melilite	40.8	3.8	27.9	27.3
208	1 633	Liquid	48.5	0.0	8.5	43.0	1.13							
		Wollastonite	48.2	0.0	0.1	51.8								
212	1 633	Liquid	46.6	2.9	6.9	43.5	1.07							
		Wollastonite	48.3	0.0	0.1	51.6								
<i>Spinel primary phase field</i>														
9	1 693	Liquid	37.8	13.6	15.1	33.4	1.13							
		Spinel	0.3	28.1	71.4	0.1								
25	1 693	Liquid	37.1	12.7	16.1	33.9	1.09							
		Spinel	0.3	28.1	70.9	0.1								
50	1 693	Liquid	36.9	14.6	14.5	33.9	1.09							
		Spinel	0.0	28.4	71.5	0.1								
58	1 713	Liquid	37.1	13.5	16.1	33.2	1.12							
		Spinel	0.3	28.4	71.0	0.2								
1	1 733	Liquid	35.7	16.2	15.1	32.9	1.09							

The liquid compositions with CaO/SiO₂ ratio close to 1.10 are used to construct liquidus isotherms of the pseudo-ternary section (CaO+SiO₂)–Al₂O₃–MgO with a fixed CaO/SiO₂ weight ratio of 1.10 as shown in **Fig. 2**.

The previous data on the CaO–SiO₂–Al₂O₃–MgO system^{6–8)} have been used in optimisation of thermodynamic software FactSage 6.2.⁹⁾ Predictions of FactSage 6.2 are shown in **Fig. 3** to compare with the present experimental data. The databases selected in FactSage 6.2 are “Fact53” and “FToxide”, and the solution species selected in calculations are “FToxide-SLAGA”, “FToxide-SPINA”, “FToxide-MeO_A”, “FToxide-bc2S”, “FToxide-ac2S”, “FToxide-Mel”, and “FToxide-Merwinite”. The previous results reported by Osborn *et al.*,⁶⁾ Cavalier and Sandra-Deudon,⁸⁾ Muan and Osborn¹⁰⁾ are also shown in Fig. 3 for the comparison. It can be seen that the present experimental results have a

Fig. 2. Liquidus isotherms of pseudo-ternary section (CaO+SiO₂)-Al₂O₃-MgO based on experimental results.

Fig. 4. A comparison in pseudo-ternary sections (CaO+SiO₂)-Al₂O₃-MgO between CaO/SiO₂ ratio of 1.10 and 1.30⁵⁾ at 1723 K.

Fig. 3. Pseudo-ternary section (CaO+SiO₂)-Al₂O₃-MgO with CaO/SiO₂ ratio of 1.10.

good agreement with previous work reported by Osborn *et al.*,⁶⁾ Cavalier and Sandra-Deudon⁸⁾ and Muan and Osborn¹⁰⁾ at 1673 K. However, obvious differences can be observed between the present data and that reported by Muan and Osborn¹⁰⁾ at 1713 and 1733 K. It can be seen that FactSage predictions show the similar overall trends as the experimental results, but the locations of the isotherms can be found significantly different. The FactSage software used the published data to optimize the databases and the accuracy of FactSage calculations rely on the accuracy of the experimental data used. The deviation of FactSage can be attributed to the limitation of the previous research techniques so that the accuracy of the data was not enough, in particular the solid solutions. Generally, the experimentally determined liquidus temperatures in the present study are approximately 20 K higher than that FactSage predictions in the melilite primary phase field. In MgO and spinel pri-

mary phase fields, the experimentally determined liquidus temperatures in the present study are usually 20 K lower than the predictions. In merwinite primary phase field, the experimentally determined liquidus temperatures agree well with the prediction values. It is noted that there is a small Ca₃Si₂O₇ primary phase field according to the FactSage predictions. However, the Ca₃Si₂O₇ primary phase was not observed in the present study. Instead, wollastonite (CaSiO₃) primary phase field present in the composition range. Additionally, the Ca₂SiO₄ primary phase was observed by the present experiments at high (CaO+SiO₂) corner, which is not shown by FactSage predictions.

To compare the effect of CaO/SiO₂ ratio on primary phase fields and liquidus temperatures, the phase boundaries and isotherm at 1723 K are shown in Fig. 4 for CaO/SiO₂ ratios of 1.10 and 1.30 respectively. It can be seen that the wollastonite primary phase field was not stable when the CaO/SiO₂ ratio is 1.30. The dicalcium silicate primary phase area expands significantly towards Al₂O₃ corner when the CaO/SiO₂ ratio is increased from 1.10 to 1.30. In contrast, the sizes of the melilite and merwinite primary phase fields are decreased with increasing CaO/SiO₂ ratio. Full liquid area represents a composition range where the slag is fully liquid phase above a given temperature. A large full liquid area indicates that the liquidus temperature of the slag is not sensitive to the variation of the composition. The full liquid area at 1723 K is described by the isotherms from different primary phase fields. It can be seen that the full liquid area at 1723 K is narrow at CaO/SiO₂ ratio of 1.30 and it is expanded significantly when the CaO/SiO₂ ratio is decreased to 1.10.

Melilite is the solid solution between akermanite (2CaO·MgO·2SiO₂) and gehlenite (2CaO·Al₂O₃·SiO₂). The distributions of MgO and Al₂O₃ between melilite and liquid are shown in Figs. 5 and 6 respectively. The solid lines in Figs. 5 and 6 are fitted from the experimental data that may have slightly different CaO/SiO₂ ratios. The predictions from FactSage 6.2 are also shown in the figures for

Fig. 5. Distribution of MgO between melilite and liquid for temperatures from 1 613 to 1 733 K.

Fig. 6. Distribution of Al_2O_3 between melilite and liquid for temperatures from 1 613 to 1 733 K.

comparison. As seen in Fig. 5, the MgO concentrations in melilite solid solution increase with increasing that in liquid up to 15 mol% MgO. At 1 673 K, the MgO concentrations in the melilite reach a maximum at 15 mol% MgO and then decrease with increasing MgO in the corresponding liquid. It can be seen that the MgO concentrations in melilite decrease with increasing temperature at a given MgO concentration in liquid. At 1 613 K, the MgO concentration in the melilite is approximately as twice as that in the corresponding liquid. At 1 673 K, the MgO concentration in the melilite is almost the same as that in the corresponding liquid. In contrast, the MgO concentration in the melilite is only half as that in the corresponding liquid at 1 733 K. The predicted MgO concentrations in melilite by FactSage 6.2 show a good agreement with experimental results at 1 613, 1 673 and 1 733 K up to 15 mol% MgO in the liquid. However, FactSage predictions show that merwinite is a stable phase at 1 673 K over 15 mol% MgO in the liquid which is different from the present results.

It can be seen from Fig. 6 that the Al_2O_3 concentrations in melilite solid solution increase with increasing that in the corresponding liquid at 1 613 and 1 673 K. The bending orientation of curves gradually change from 1 613 to 1 733 K which reflects the same shape of the isotherms in the melilite primary phase field. Similar retrograde curves were also reported at CaO/SiO₂ ratio of 1.30 from 1 723 to 1 773 K.⁵⁾ The Al_2O_3 concentration in melilite is much

higher than that in the corresponding liquid phase at a given temperature. It is interesting to see that FactSage can predict the general trend of the distributions but the values are significantly different which may explain the difference in liquidus temperatures predicted.

3.2. Application of Phase Diagram in Ironmaking Process

3.2.1. Effect of MgO on Liquidus Temperature

Recently BF operation is facing the challenges to lower the cost by increased utilization of pulverized coal injection and low-grade ores, and reduced flux addition such as MgO. These changes would result in higher Al_2O_3 or lower MgO in the slag.^{11–13)} The Figs. 7 and 8 were redrawn in the form of pseudo-binary section for better understanding from pseudo-ternary phase diagram of Fig. 3. The data was collected from Fig. 3 when fixing the Al_2O_3 concentration of 15% and 20%, or MgO concentration of 5% and 10%. Figure 7 shows the relationship between the liquidus temperatures and MgO concentration at fixed Al_2O_3 of 15 and 20 wt% and CaO/SiO₂ ratio of 1.10 and 1.30. 15 wt% Al_2O_3 in slag represents an average in the current BF operations and 20 wt% Al_2O_3 in slag is a result of low grade iron ore utilization. It can be seen from Fig. 7 that the stable primary phase field is melilite at low MgO concentrations and spinel at high MgO concentrations. The liquidus temperatures always increase with increasing MgO concentration in the spinel primary phase field. In the melilite primary phase field the liquidus temperatures have different behaviours depending on the Al_2O_3 concentration and CaO/SiO₂ ratio. It can be seen that at 15 wt% Al_2O_3 and CaO/SiO₂ ratio of 1.10, the liquidus temperatures first increase rapidly and decrease with increasing MgO. At 20 wt% Al_2O_3 and CaO/SiO₂ ratio of 1.10, the trend of the liquidus temperature changes with MgO is similar but it is less sensitive than 15 wt% Al_2O_3 . At 20 wt% Al_2O_3 and CaO/SiO₂ ratio of 1.30, the liquid temperatures do not change with MgO at MgO below 5 wt%. However, the liquid temperatures decrease with increasing MgO above 5 wt%. The stability of the spinel phase seems not sensitive to CaO/SiO₂ ratio but to the Al_2O_3 concentration. For example, at 20 wt% Al_2O_3 , the boundary between the melilite and spinel primary phase fields is the same at 10 wt% MgO for the CaO/SiO₂ ratios of 1.10 and 1.30. However, at the same CaO/SiO₂ ratio of 1.10, the spinel phase will be formed above 10 and 13 wt% MgO for the Al_2O_3 concentrations 20 and 15 wt% respectively. The liquidus temperatures in the melilite primary phase field increase with increasing both Al_2O_3 concentration and CaO/SiO₂ ratio. It seems that the increment of the melilite liquidus temperature with CaO/SiO₂ ratio is more sensitive at lower MgO concentrations. In contrast, the liquidus temperatures in the spinel primary phase field are more sensitive to the Al_2O_3 concentration and less sensitive to the CaO/SiO₂ ratio. The accurate information given in the present study will provide useful guide to BF operators to work at temperatures high enough to avoid the precipitation of solid phases when complex feeds are used in ironmaking.

3.2.2. Effect of Al_2O_3 on Liquidus Temperature

Figure 8 shows the relationship between liquidus temperature and Al_2O_3 concentration at fixed MgO of 5 and

Fig. 7. The effect of MgO on the liquidus temperature in which $\text{Al}_2\text{O}_3=15$ and 20 wt%, $\text{CaO}/\text{SiO}_2=1.10$ and 1.30.

Fig. 8. The effect of Al_2O_3 on the liquidus temperature in which $\text{MgO}=5$ and 10 wt%, $\text{CaO}/\text{SiO}_2=1.10$ and 1.30.

10 wt% and CaO/SiO_2 ratio of 1.10 and 1.30. 10 wt% MgO in slag represents an average in the current operations and 5 wt% MgO in slag is a result of low slag rate operation. It can be seen that Al_2O_3 has significant influence in primary phase field and liquidus temperature in the composition range investigated. Dicalcium silicate and merwinite are the major stable phases at low Al_2O_3 concentrations and melilite is the major stable phase at high Al_2O_3 concentrations. Wollastonite (CaSiO_3) also appears at 5 wt% MgO and CaO/SiO_2 ratio of 1.10, but disappears when the MgO concentration is 10 wt%. The spinel also appears at 10 wt% MgO and CaO/SiO_2 ratio of 1.10. In the melilite and spinel primary phase fields the liquidus temperatures increase significantly with increasing Al_2O_3 concentration. In contrast, the liquidus temperatures in the primary phase fields of dicalcium silicate, merwinite and wollastonite decrease significantly with increasing Al_2O_3 concentration. At CaO/SiO_2 ratio of 1.10, the liquidus temperature with 5 wt% MgO is lower than that with 10 wt% MgO below 16 wt% Al_2O_3 . At 5

wt% MgO concentration for low slag volume operation, the liquidus temperatures are increased by approximate 40 K in the melilite primary phase field above 12 wt% Al_2O_3 when the CaO/SiO_2 ratio increases from 1.10 to 1.30. Clearly the operating range of Al_2O_3 where the slag is fully liquid is much wider at CaO/SiO_2 ratio of 1.10. The BF operation at high CaO/SiO_2 ratio and low MgO concentration will be very difficult.

4. Conclusions

The phase equilibria and liquidus temperatures in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system with CaO/SiO_2 ratio of 1.10 have been experimentally determined in the composition range related to blast furnace slags. Providing a fixed MgO or Al_2O_3 concentration closed to the composition of industrial slag, the liquidus temperatures increases with increasing Al_2O_3 concentration, but not sensitive with increasing MgO concentration. It is confirmed that low-slag volume BF operation can be achieved by decreasing MgO concentration at certain conditions. Extensive solid solutions of melilite have been accurately determined that will provide invaluable data for optimisation of thermodynamic database.

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