Phase Equilibria in the CaO–SiO₂–Al₂O₃–MgO System with CaO/SiO₂ Ratio of 1.3 Relevant to Iron Blast Furnace Slags

Xiaodong MA,^{1)*} Geoff WANG,¹⁾ Shengli WU,²⁾ Jinming ZHU²⁾ and Baojun ZHAO¹⁾

1) School of Chemical Engineering, The University of Queensland, Brisbane, 4072 Australia.

2) Baoshan Iron and Steel (Baosteel) Co. Ltd, Shanghai, 201900 China.

(Received on May 15, 2015; accepted on July 22, 2015; J-STAGE Advance published date: September 8, 2015)

Phase equilibria and liquidus temperatures in the CaO–SiO₂–Al₂O₃–MgO system with CaO/SiO₂ weight ratio of 1.30 have been experimentally determined by means of high temperature equilibration and quenching technique followed by electron probe X-ray microanalysis. Isotherms between 1 723 and 1 773 K were determined in the primary phase fields of melilite, dicalcium silicate, spinel, merwinite and periclase that are relevant to ironmaking slags. Effects of Al₂O₃, MgO and CaO/SiO₂ ratio on the liquidus temperatures have been discussed. Compositions of the solid phases corresponding to the liquidus have been accurately measured that will be used for development of the thermodynamic database.

KEY WORDS: liquidus temperature; CaO–SiO₂–Al₂O₃–MgO system; BF slag; EPMA.

1. Introduction

The blast furnace (BF) process continues to be the principal technique used for ironmaking across the world. Recently, with the increasing trend of utilization of low grade iron ores, and injection of coal, the BF operation confronts the new challenge of low gas permeability and formation of hearth accretion.^{1–3)} To ease this issue, accurate data on the phase diagram of the BF slag are required. The oxide system CaO–SiO₂–Al₂O₃–MgO forms a base for ironmaking slags. A series of pseudo-ternary phase diagrams sections in the system CaO–SiO₂–Al₂O₃–MgO have been summarised in Slag Atlas⁴⁾ at fixed concentrations of Al₂O₃ or MgO that are mainly based on the works reported by Osborn *et al.*,⁵⁾ Gutt and Russel⁶⁾ and Cavalier and Sandra-Deudon.⁷⁾ However, the isotherms reported were in 100 degrees interval and there are significant gaps in the composition range related to the ironmaking slags. In addition, the pseudo-ternary sections reported as CaO–MgO–SiO₂ at fixed Al₂O₃ or Al₂O₃–CaO–SiO₂ at fixed MgO cannot accurately predict the effect of MgO/Al₂O₃ on liquidus temperature which is important for the current BF operations. It has also been demonstrated in recent studies that significant differences are observed for the phase diagrams in the Al₂O₃–CaO–MgO–SiO₂ system between the new results^{8–12)} and those reported in the early research.^{5–7)} On the other hand, solid solutions presented in the system Al₂O₃–CaO–MgO–SiO₂, in particular melilite phase in which industrial slags are operated, are important for optimisation of the thermodynamic database. These compositions of solid solutions could not be accurately measured by previous techniques. Hence,

accurate phase equilibria data are of importance for both industrial and scientific interests.

The BF slags can be classified to be primary slags, bosh slags and final slags during descent in the BF. Most of the final BF slags have the weight ratio of CaO/SiO₂ between 1.10 and 1.30.^{13–15)} The bosh slag in the upstream of the hearth generally has a higher CaO/SiO₂ ratio than the final slag. In the current work, the liquidus surfaces in the CaO–SiO₂–Al₂O₃–MgO system with CaO/SiO₂ ratio of 1.30 have been investigated that are relevant to BF bosh and final slags.

2. Experimental

2.1. Selection of Pseudo-ternary System

The selection of an appropriate pseudo-ternary section in a multi-component system is important for efficient research and for easy use of the experimental information in industrial practice. In the present study, the phase diagram is presented in the form of pseudo-ternary section MgO–Al₂O₃–(CaO+SiO₂) with CaO/SiO₂ of 1.30, as shown in **Fig. 1**. There are a couple of advantages for choosing MgO, Al₂O₃ and (CaO+SiO₂) as the end members of the pseudo-ternary section.

- With increasing usage of low grade iron ore, effects of Al₂O₃ and MgO on liquidus temperatures are important and can be examined accurately.
- CaO/SiO₂ ratio (binary basicity) is commonly used by process operators to control slag composition. The CaO/SiO₂ ratio does not change significantly in a particular plant. The presentation of the experimental results in the form of this pseudo-ternary section means that the information can be readily used by plant engineers to better understand and control the

* Corresponding author: E-mail: x.ma@uq.edu.au

DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2015-263>

Fig. 1. The pseudo-ternary section with $\text{CaO}/\text{SiO}_2 = 1.30$ in the composition tetrahedron $\text{CaO}-\text{SiO}_2-\text{MgO}-\text{Al}_2\text{O}_3$.

process.

- (c) Ternary basicity $(\text{CaO}+\text{MgO})/\text{SiO}_2$ is important to evaluate sulphur capacity and viscosity of the slag. The pseudo-ternary phase diagram $\text{MgO}-\text{Al}_2\text{O}_3-(\text{CaO}+\text{SiO}_2)$ enables the liquidus temperatures to be analysed as a function of $(\text{CaO}+\text{MgO})/\text{SiO}_2$ ratio at fixed Al_2O_3 concentrations.

2.2. Experimental Procedure

The experimental method used in the present study involves high temperature equilibration, quenching and electron probe X-ray microanalysis (EPMA).^{16,17} High-purity reagent powders of Al_2O_3 , SiO_2 , MgO , CaCO_3 were used as starting materials and thoroughly mixed in an agate mortar after weighing. The mixtures were pelletized prior to equilibration, and approximately 0.2 g samples were placed in graphite crucibles at predetermined temperatures in a high-purity Ar atmosphere. The experiments were carried out using a vertical electric resistance furnace. The sample was equilibrated for times from 8 to 24 hours depending on the composition and temperature. 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 thermocouple was calibrated periodically using a reference thermocouple supplied by National Measurement Laboratory (CSIRO, Melbourne, Australia). The temperature of the furnace was controlled within 2 K and overall temperature uncertainty is within 5 K.

The sample inside a graphite crucible was first attached to a Mo wire and placed in the cool zone of the furnace. The bottom end of the recrystallised alumina reaction tube was sealed with a glass window. After ultrahigh purity Ar (total impurities ≤ 5 ppm, oxygen ≤ 1 ppm) was passed through the furnace tube for 30 minutes to remove the air, the sample was raised into the hot zone to a position adjacent to the thermocouple. The experiment was usually carried out in two steps. The first step was to premelt the sample at a temperature higher than the anticipated liquidus to ensure that equilibrium was approached through precipitation from the melt. The sample was then equilibrated at the desired temperature for a time sufficient to achieve equilibrium.

2.3. Sample Examination

The samples were directly quenched into water after the equilibration, then dried, mounted and polished for metallographic analysis. The rapid quenching of these silicate slags to room temperature converted the liquid phase to homogeneous glass. The crystalline solids present at temperature were also retained on quenching without change in their shapes and compositions. 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). An accelerating voltage of 15 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with JXA-8200 was applied. The standards used for EPMA from Charles M. Taylor Co. (Standard, CA) include alumina (Al_2O_3) for Al, magnesia (MgO) for Mg, wollastonite (CaSiO_3) for Ca and Si. The average accuracy of the EPMA measurements is within 1 wt%.

3. Results and Discussions

3.1. Description of the Pseudo-ternary Section

Over 150 experiments have been carried out in the $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}$ system with the CaO/SiO_2 weight ratio of 1.30. Dicalcium silicate, spinel, merwinite, periclase and melilite were found to be the primary phases in the composition range investigated. In the primary phase fields of dicalcium silicate, merwinite and melilite, CaO/SiO_2 ratio in the liquid was usually lower than 1.30 as CaO/SiO_2 ratio in these solid phases are higher than 1.30. The difficulty in controlling CaO/SiO_2 ratio at 1.30 can be solved in preparing initial slags with slightly higher CaO/SiO_2 ratios. The compositions of liquid and solids measured by EPMA covering Al_2O_3 concentration up to 35 wt%, MgO up to 20 wt%, are presented in Table 1 and plotted in Fig. 2. The liquidus with CaO/SiO_2 ratio much lower than 1.30 were not used in constructing phase diagram. Typical microstructures observed in the quenched samples are presented in Fig. 3. Figure 3(a) shows the equilibrium of liquid with melilite at temperature. Figures 3(b) and 3(c) show the equilibrium of liquid with dicalcium silicate and liquid with spinel respectively. Figure 3(d) shows the equilibrium of liquid with merwinite and dicalcium silicate. EPMA measurements show that the compositions of dicalcium silicate (Ca_2SiO_4), spinel ($\text{MgO}\cdot\text{Al}_2\text{O}_3$), merwinite ($3\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) and periclase (MgO) are close to their stoichiometry. Melilite is the solid solution between akermanite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) and gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$).

The data given in Table 1 have been used to construct liquidus isotherms of the pseudo-ternary section $(\text{CaO}+\text{SiO}_2)-\text{Al}_2\text{O}_3-\text{MgO}$ with a fixed CaO/SiO_2 weight ratio of 1.30, as shown in Fig. 4. The results reported by Osborn *et al.*,⁵ Cavalier and Sandra-Deudon,⁷ Muan and Osborn¹⁸ are also given in Fig. 4 for comparison. The present experimental results show general agreement with previous works. The liquidus temperatures in Ca_2SiO_4 primary phase field reported by Osborn *et al.*⁵ are much higher than the present results. In addition, predictions of FactSage 6.2¹⁹ are also shown in the figure for comparison. The databases selected

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

Table 1. Experimental results in the system CaO–SiO ₂ –Al ₂ O ₃ –MgO with CaO/SiO ₂ ratio.								8	1 673	Liquid	45.5	5.6	11.0	37.9	1.20						
Experiment No.	Temperature (K)	Phases	Composition (wt%)				CaO/SiO ₂	21	1 703	Melilite	41.0	5.8	22.5	30.8	1.26						
			CaO	MgO	Al ₂ O ₃	SiO ₂				Liquid	47.4	0.0	15.1	37.5							
Liquid								12	1 723	Melilite	41.5	0.0	36.4	22.2	1.23						
33	1 693	Liquid	48.6	0.0	13.0	38.3	1.27	Liquid	45.9	0.0	16.7	37.4									
31	1 703	Liquid	46.0	5.4	11.9	36.7	1.25	Melilite	41.0	0.0	36.8	22.1	9	1 723	Liquid	44.6	5.4	14.5	35.5	1.26	
118	1 703	Liquid	40.1	12.0	18.0	29.9	1.34	Melilite	41.0	2.8	29.8	26.3		Liquid	44.6	5.4	14.5	35.5	1.26		
30	1 723	Liquid	40.4	10.1	17.3	32.1	1.26	123	1 723	Melilite	41.0	2.8	30.1	26.1	Liquid	39.4	10.9	18.3	31.3	1.26	
10	1 723	Liquid	46.1	5.4	12.0	36.5	1.26	Melilite	41.0	2.8	30.1	26.1	52	1 723	Liquid	44.0	7.5	14.5	34.0	1.29	
14	1 723	Liquid	48.6	0.0	13.1	38.3	1.27	Melilite	41.3	3.0	28.8	26.9	Liquid	44.0	7.5	14.5	34.0	1.29			
29	1 723	Liquid	48.1	0.0	14.6	37.3	1.29	133	1 723	Melilite	41.3	3.0	28.8	26.9	Liquid	44.0	7.5	14.5	34.0	1.29	
12	1 723	Liquid	47.6	2.0	13.8	36.6	1.30	Liquid	48.0	0.0	14.9	37.1	1.29	132 <th>1 723</th> <td>Melilite</td> <td>41.0</td> <td>0.0</td> <td>36.9</td> <td>22.1</td> <td rowspan="2">1.30</td>	1 723	Melilite	41.0	0.0	36.9	22.1	1.30
53	1 723	Liquid	40.1	10.8	18.5	30.6	1.31	Melilite	41.0	0.0	36.9	22.1	Liquid	47.4	2.0	14.1	36.5				
121	1 723	Liquid	45.5	5.6	14.2	34.7	1.31	122	1 723	Liquid	47.4	2.0	14.1	36.5	Melilite	40.9	1.4	33.4	24.2	1.30	
109	1 723	Liquid	39.3	10.4	20.5	29.8	1.32	Melilite	40.9	1.4	33.4	24.2	Liquid	41.9	9.7	16.2	32.2				
104	1 723	Liquid	48.4	0.0	14.9	36.6	1.32	39	1 723	Melilite	40.9	2.9	29.9	26.4	Liquid	41.9	9.7	16.2	32.2	1.30	
40	1 723	Liquid	40.7	11.9	17.4	30.0	1.36	Liquid	41.9	9.7	16.2	32.2	Liquid	48.8	0.0	14.4	36.7	1.33			
35	1 733	Liquid	44.4	5.3	14.8	35.5	1.25	41	1 723	Melilite	40.9	0.0	37.2	21.9	Melilite	48.8	0.0	14.4	36.7	1.33	
36	1 743	Liquid	45.7	0.0	18.3	35.9	1.27	Melilite	40.9	0.0	37.2	21.9	Liquid	42.8	9.3	15.8	32.1				
26	1 753	Liquid	49.8	0.0	11.1	39.1	1.27	22	1 733	Liquid	42.8	9.3	15.8	32.1	Melilite	42.8	9.3	15.8	32.1	1.33	
37	1 753	Liquid	38.6	10.1	21.2	30.1	1.28	Melilite	41.2	2.7	30.3	25.8	Liquid	46.3	0.0	16.9	36.8	1.26			
159	1 753	Liquid	46.7	1.9	17.4	34.0	1.37	119	1 753	Liquid	46.3	0.0	16.9	36.8	Melilite	46.3	0.0	16.9	36.8	1.26	
160	1 753	Liquid	45.7	3.7	17.4	33.2	1.38	Melilite	41.3	0.0	36.5	22.2	Liquid	46.3	0.0	16.9	36.8	1.26			
161	1 753	Liquid	43.9	5.4	18.7	31.9	1.37	163	1 753	Melilite	41.3	0.0	36.5	22.2	Liquid	41.3	0.0	36.5	22.2	1.31	
166	1 753	Liquid	43.2	12.2	12.4	32.2	1.34	Liquid	38.0	9.6	23.5	29.0	Liquid	38.0	9.6	23.5	29.0	1.31			
188	1 753	Liquid	42.9	12.0	12.3	32.9	1.31	181	1 753	Melilite	41.1	1.8	32.8	24.3	Melilite	41.1	1.8	32.8	24.3	1.37	
189	1 753	Liquid	49.9	0.0	11.9	38.1	1.31	Melilite	41.1	1.8	32.8	24.3	Liquid	47.6	0.0	17.8	34.6	1.37			
190	1 753	Liquid	48.2	2.1	12.4	37.3	1.29	182	1 753	Liquid	42.0	0.0	36.4	21.6	Liquid	47.6	0.0	17.8	34.6	1.37	
192	1 753	Liquid	44.9	8.6	12.1	34.4	1.31	Melilite	42.0	0.0	36.4	21.6	Liquid	47.6	0.0	17.8	34.6	1.37			
7	1 773	Liquid	49.5	0.0	11.2	39.3	1.26	183	1 753	Liquid	45.8	0.0	18.2	36.0	Liquid	47.6	0.0	17.8	34.6	1.37	
50	1 773	Liquid	37.2	13.8	20.1	29.0	1.28	Melilite	41.4	0.0	36.6	21.9	Liquid	45.8	0.0	18.2	36.0	1.28			
126	1 773	Liquid	41.5	5.0	21.2	32.2	1.29	184	1 753	Liquid	41.4	0.0	36.6	21.9	Liquid	45.8	0.0	18.2	36.0	1.28	
63	1 773	Liquid	38.6	7.6	24.0	29.8	1.30	Melilite	44.9	1.8	18.2	35.1	Liquid	44.9	1.8	18.2	35.1	1.28			
62	1 773	Liquid	40.0	6.9	22.4	30.7	1.30	185	1 753	Melilite	40.9	0.9	34.6	23.6	Liquid	44.9	1.8	18.2	35.1	1.28	
78	1 773	Liquid	44.0	9.9	12.4	33.7	1.30	Melilite	40.9	0.9	34.6	23.6	Liquid	44.1	3.5	17.6	34.9	1.26			
127	1 773	Liquid	38.6	6.0	26.0	29.5	1.31	186	1 753	Liquid	44.1	3.5	17.6	34.9	Liquid	44.1	3.5	17.6	34.9	1.26	
79	1 773	Liquid	42.8	12.1	12.5	32.6	1.31	Melilite	41.3	1.5	32.9	24.3	Liquid	44.1	3.5	17.6	34.9	1.26			
97	1 773	Liquid	38.2	6.9	25.8	29.0	1.32	187	1 753	Liquid	42.6	5.2	18.3	33.9	Liquid	42.6	5.2	18.3	33.9	1.26	
96	1 773	Liquid	39.6	6.0	24.3	30.0	1.32	Melilite	41.1	1.8	32.3	24.8	Liquid	42.6	5.2	18.3	33.9	1.26			
128	1 773	Liquid	36.5	5.9	30.0	27.6	1.32	188	1 773	Melilite	41.1	1.8	32.3	24.8	Liquid	42.6	5.2	18.3	33.9	1.26	
110	1 773	Liquid	36.7	7.5	28.1	27.6	1.33	Melilite	41.1	1.8	32.3	24.8	Liquid	40.5	7.1	19.7	32.7	1.24			
137	1 773	Liquid	38.0	3.9	29.6	28.5	1.33	189	1 753	Liquid	40.5	7.1	19.7	32.7	Melilite	40.5	7.1	19.7	32.7	1.24	
43	1 773	Liquid	38.6	8.4	24.7	28.3	1.36	Melilite	41.1	2.0	31.9	25.0	Liquid	40.5	7.1	19.7	32.7	1.24			
Liquid with one oxide solid								186	1 773	Melilite	41.1	2.0	31.9	25.0	Liquid	40.5	7.1	19.7	32.7	1.24	
Meliite primary phase field								Melilite	41.1	2.0	31.9	25.0	Liquid	40.5	7.1	19.7	32.7	1.24			
15	1 673	Liquid	47.4	0.0	13.6	39.0	1.21	164	1 773	Liquid	37.1	0.0	31.6	31.3	Liquid	43.4	0.0	21.6	35.0	1.24	
		Melilite	41.1	0.0	36.5	22.3		Melilite	41.9	0.0	36.5	21.6	Liquid	37.1	0.0	31.6	31.3	1.19			
								Liquid	40.8	4.8	20.8	33.5	1.22	138 <th>1 773</th> <td>Melilite</td> <td>41.9</td> <td>0.0</td> <td>36.5</td> <td>21.6</td> <td rowspan="2">1.19</td>	1 773	Melilite	41.9	0.0	36.5	21.6	1.19
								Melilite	41.1	1.7	32.8	24.4	Liquid	40.8	4.8	20.8	33.5	1.22			
														6 <th>1 773</th> <td>Melilite</td> <td>41.1</td> <td>1.7</td> <td>32.8</td> <td>24.4</td> <td rowspan="2">1.19</td>	1 773	Melilite	41.1	1.7	32.8	24.4	1.19
														Liquid	43.4	0.0	21.6	35.0	1.24		
														Melilite	41.0	0.0	37.2	21.9		1.29	
														Liquid	45.1	0.0	19.9	35.0	1.29		
														Melilite	40.9	0.0	37.3	21.8		1.29	
														Melilite	40.9	0.0	37.3	21.8			

© 2015 ISIJ

Liquid with more oxide solids							
82	1 723	Liquid	44.6	8.5	11.8	35.1	1.27
		Dicalcium silicate	61.3	3.2	0.2	35.2	
		Merwinite	51.6	12.0	0.1	36.3	
87	1 723	Liquid	44.6	8.4	11.7	35.3	1.26
		Dicalcium silicate	61.3	3.3	0.2	35.2	
		Merwinite	51.5	12.2	0.1	36.3	
88	1 723	Liquid	44.4	8.6	12.1	35.0	1.27
		Dicalcium silicate	61.5	3.3	0.2	35.0	
		Merwinite	51.4	12.2	0.1	36.4	
91	1 773	Liquid	43.7	11.9	10.7	33.6	1.30
		Dicalcium silicate	60.4	4.3	0.2	35.3	
		Merwinite	51.3	12.1	0.1	36.4	
102	1 693	Liquid	45.6	5.8	11.2	37.4	1.22
		Dicalcium silicate	62.0	2.3	0.3	35.3	
		Melilite	45.2	3.8	21.4	29.6	
59	1 673	Liquid	45.4	6.3	9.7	38.6	1.18
		Dicalcium silicate	61.5	2.7	0.3	35.5	
		Melilite	41.2	6.5	20.1	32.3	
55	1 673	Liquid	47.4	2.7	11.0	39	1.22
		Dicalcium silicate	63.3	1.1	0.4	35.1	
		Melilite	41.4	2.9	29.2	26.5	
5	1 673	Liquid	48.3	0.0	12.6	39	1.24
		Dicalcium silicate	65.2	0.0	0.0	34.8	
		Melilite	40.9	0.0	36.7	22.4	
107	1 723	Liquid	46.1	5.2	13.2	35.4	1.30
		Dicalcium silicate	62.6	2.1	0.3	35.1	
		Melilite	41.0	2.8	30.1	26.1	
72	1 723	Liquid	38.6	14.8	16.1	30.6	1.26
		Periclase	0.5	98.9	0.5	0.1	
		Merwinite	50.9	12.4	0.1	36.6	
81	1 773	Liquid	42.0	14.4	11.2	32.5	1.29
		Periclase	0.3	99.0	0.6	0.0	
		Merwinite	51.1	12.3	0.1	36.5	
77	1 723	Liquid	39.4	14.5	15.7	30.4	1.30
		Periclase	0.3	98.9	0.8	0.0	
		Merwinite	50.9	12.4	0.1	36.6	
116	1 723	Liquid	39.2	11.5	18.3	31.0	1.26
		Spinel	0.7	28.0	70.9	0.4	
		Melilite	40.7	2.5	31.1	25.7	
134	1 693	Liquid	45.1	7.1	11.0	36.9	1.22
		Merwinite	51.6	12.0	0.1	36.3	

		Melilite	41.3	5.6	22.6	30.5	
111	1 703	Liquid	40.0	11.3	14.7	34	1.18
		Merwinite	50.3	12.4	0.1	37.1	
		Melilite	40.5	4.2	26.5	29.0	
		Dicalcium silicate	64.2	0.0	0.4	35.4	
101	1 723	Liquid	37.7	11.8	19.3	31.1	1.21
		Spinel	0.1	28.2	71.7	0.0	
		Merwinite	40.8	2.9	30.1	26.3

Fig. 2. Experimental composition range in the CaO–SiO₂–MgO–Al₂O₃ system.

in FactSage 6.2 are “Fact53” and “FToxide”, and the solutions species selected in calculation are “FToxide-SLAGA”, “FToxide-SPINA”, “FToxide-MeO_A”, “FToxide-bC2S”, “FToxide-aC2S”, “FToxide-Mel_”, and “FToxide-Merwinite”. It can be seen that FactSage predictions show the similar trends as the experimental results, but the locations of the isotherms are significantly different. Experimentally determined liquidus temperatures in the spinel and Ca₂SiO₄ primary phase fields are approximately 50 K lower than those predicted by FactSage 6.2. However, in merwinite primary phase field, the experimentally determined liquidus temperatures are approximately 50 K higher than the predictions. A significant difference is that the experimentally determined merwinite phase area is larger than the FactSage predictions. This significant difference may come from the lack of the thermodynamics data in merwinite primary phase field. In melilite primary phase field, the experimentally determined liquidus temperatures are usually 20 K different from predicted values.

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. As seen in Fig. 5, the MgO concentrations in melilite solid solution first increase with increasing MgO concentration in liquid, and then slightly decrease after reaching the maximum. It is also found that the MgO concentrations in melilite decrease with increasing temperature and the predicted MgO concentrations in melilite by FactSage 6.2 are higher than the experi-

Fig. 3. Typical microstructures of slags quenched from (a) melilite, (b) Ca_2SiO_4 and (c) spinel primary phase fields and (d) merwinite and Ca_2SiO_4 phase boundary.

Fig. 4. Pseudo-ternary section $(\text{CaO}+\text{SiO}_2)\text{-Al}_2\text{O}_3\text{-MgO}$ with CaO/SiO_2 ratio of 1.30.

Fig. 5. Distribution of MgO between melilite and liquid for temperature between 1723 and 1773 K.

mental results. As seen in Fig. 6, the distribution of Al_2O_3 between melilite and liquid is complicated. For a given Al_2O_3 concentration in the liquid, there are two corresponding melilite compositions. Generally the Al_2O_3 concentration in melilite is higher than that in the liquid phase. It is interesting to see that FactSage can predict the general trend of the distributions but the values are significantly different which can explain the difference in liquidus temperatures.

3.2. Comparison of the System $(\text{CaO}+\text{SiO}_2)\text{-Al}_2\text{O}_3\text{-MgO}$ with CaO/SiO_2 Ratios of 1.10 and 1.30

In most case, the ironmaking BF slags have the $\text{CaO}/$

SiO_2 ratio in the range of 1.10 to 1.30 in practical operations. The isotherms in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system with CaO/SiO_2 ratio of 1.10 reported by Zhang *et al.*¹⁴⁾ are compared with the present work with CaO/SiO_2 ratio of 1.30 as shown in Fig. 7. The melilite primary phase field dominates in the composition range studied at CaO/SiO_2 ratio of 1.10. However, when the CaO/SiO_2 ratio is increased to 1.30, dicalcium silicate becomes more stable and its primary phase field shifts towards high Al_2O_3 direction. The liquidus temperatures are also significantly affected with increasing CaO/SiO_2 ratio and the details will be discussed in the following sections.

Fig. 6. Distribution of Al_2O_3 between melilite and liquid for temperature between 1723 and 1773 K.

Fig. 7. Comparison of the sections $(\text{CaO}+\text{SiO}_2)\text{-Al}_2\text{O}_3\text{-MgO}$ with CaO/SiO_2 ratio of 1.30 and 1.10.^[14]

3.3. Application of Pseudo-binary Phase Diagrams

Recently BF operation is facing the challenges to lower the cost by the increase of pulverized coal injection, utilization of low-grade ores and reduction of slag volume. These changes could result in higher Al_2O_3 or lower MgO in the slag.²⁰⁻²²⁾ Figures 8(a) and 8(b) show the relationship between the liquidus temperatures and MgO concentration at fixed Al_2O_3 of 15 and 20 wt%. 15 wt% Al_2O_3 in slag represents an average in the current operation and 20 wt% Al_2O_3 in slag is a result of low grade iron ore utilization. It can be seen from Fig. 8(a) that with 15 wt% Al_2O_3 in slag, melilite and MgO are the primary phases in the composition range up to 15 wt% MgO and CaO/SiO_2 ratio of 1.1. The liquidus temperatures in MgO primary phase field increase dramatically with increasing MgO concentration. The MgO concentration (15 wt%) where MgO starts to form is the up limit. On the other hand, it can be seen that decrease of MgO from 10 wt% to 5 wt% can decrease the liquidus temperature by 40 K. At CaO/SiO_2 ratio of 1.3 merwinite primary phase field appears between the melilite and MgO primary phase fields. The liquidus temperatures in the melilite primary phase field has a maximum at 7 wt% MgO . When low grade iron ore is used the Al_2O_3 concentration in

(a) 15% Al_2O_3

(b) 20% Al_2O_3

Fig. 8. The effect of MgO on the liquidus temperature in which $\text{Al}_2\text{O}_3 = 15$ and 20 wt%.

the slag can be as high as 20 wt%. It can be seen from Fig. 8(b) that spinel phase will appear at high MgO concentration. The liquidus temperatures in the spinel primary phase field increase significantly with increasing MgO concentration. At high Al_2O_3 (20 wt%) and high CaO/SiO_2 ratio (1.3) decrease of MgO from 10 to 5 wt% can cause significant increase of the liquidus temperature. The accurate information given here will provide useful guide to BF operators to work at temperatures high enough to avoid the precipitation of solid phases.

Figures 9(a) and 9(b) show the relationship between the liquidus temperatures and Al_2O_3 concentration at fixed MgO of 5 and 10 wt% respectively. 10 wt% MgO in slag represents an average in the current operation and 5 wt% MgO in slag is a result of low slag rate operation. It can be seen that Al_2O_3 has strong influence in liquidus temperatures in all primary phase fields present in the composition range investigated. 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 dicalcium silicate and merwinite primary phase fields decrease significantly with increasing Al_2O_3 concentration.

Fig. 9. The effect of Al_2O_3 on the liquidus temperature in which $\text{MgO} = 5$ and 10 wt%.

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 1.30 have been experimentally determined from 1723 to 1773 K. Effects of CaO/SiO_2 ratio, Al_2O_3 and MgO concentrations on liquidus temperature have been presented.

Extensive solid solutions of melilite have been accurately determined that will provide invaluable data for optimisation of thermodynamic database.

Acknowledgements

The authors would like to thank Ms. Jie Yu for the lab assistance in the high temperature experiments and financial support from Baosteel through The Baosteel-Australia Joint Research and Development Centre. The authors also would like to thank Mr Ron Rasch and Ms Ying Yu in Centre for Microscopy and Microanalysis (CMM) for technical support of EPMA and SEM.

REFERENCES

- 1) M. Hino, T. Nagasaka, A. Katsumata, K. I. Higuchi, K. Yamaguchi and N. Kon-No: *Metall. Trans. B*, **30** (1999), 671.
- 2) M. Matsumura, M. Hoshi and T. Kawaguchi: *ISIJ Int.*, **45** (2005), 594.
- 3) V. Shatokha and O. Velychko: *High Temp. Mater. Proc.*, **31** (2012), 215.
- 4) V. D. Eisenhuttenleute: *Slag Atlas*, Verlag Stahleisen GmbH, Düsseldorf, (1995), 156.
- 5) E. F. Osborn, R. C. DeVries, K. H. Gee and H. M. Kraner: *Trans. AIME, J. Met.*, **200** (1954), 33.
- 6) W. Gutt and A. D. Russel: *J. Mater. Sci.*, **12** (1977), 1869.
- 7) G. Cavalier and M. Sandrea-Deudon: *Rev. Metall.*, **57** (1960), 1143.
- 8) B. Zhao, E. Jak and P. C. Hayes: International Congress on the Science and Technology of Ironmaking (ICSTI '09), Chinese Society for Metals, Shanghai, (2009), 1176.
- 9) F. Dahl, J. Brandberg and S. Du: *ISIJ Int.*, **46** (2006), 614.
- 10) J. Gran, Y. Wang and S. Du: *Calphad*, **35** (2011), 249.
- 11) J. Gran, B. Yan and S. Du: *Metall. Trans. B*, **42** (2011), 1008.
- 12) R. V. Hargave and M. R. K. Rao: *Trans. Indian Inst. Met.*, **32** (1979), 511.
- 13) H. Kim, H. Matsuura, F. Tsukihashi, W. Wang, D. J. Min and I. Sohn: *Metall. Trans. B*, **44** (2013), 5.
- 14) D. Zhang, E. Jak, P. Hayes and B. Zhao: 4th Annual High Temperature Processing Symp., Swinburne University of Technology, Melbourne, (2012), 17.
- 15) Q. Y. Yu, L. L. Zhang and C. C. Lin: *Baosteel Technol.*, **3** (2002), 37.
- 16) B. Zhao, E. Jak and P. Hayes: *Metall. Trans. B*, **42** (2011), 490.
- 17) B. Zhao, E. Jak and P. Hayes: *Metall. Trans. B*, **42** (2011), 56.
- 18) A. Muan and E. F. Osborn: *Phase Equilibria among Oxides in Steel-making*, Addison-Wesley Publishing Company, Inc., Boston, (1965), 95.
- 19) X. Ma: FactSage, version 6.2, <http://www.factsage.com/>, (accessed 2013-03-15).
- 20) K. Ishii and Y. Kashiwaya: *Advanced Pulverized Coal Injection Technology and Blast Furnace Operation*, Pergamon, Oxford, (2000), 133.
- 21) W. H. Kim, I. Sohn and D. J. Min: *Steel Res. Int.*, **81** (2010), 735.
- 22) P. Zhao, L. Zhang, B. Sun and H. Zhang: *Sci. Technol. Inf.*, **5** (2010), 49.