Experimental Determination of the Phase Diagram for CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ System

Junjie SHI,^{1,2)} Lifeng SUN,^{1,2)*} Jiyu QIU,^{1,2)} Zhaoyun WANG,^{1,2)} Bo ZHANG^{1,2)} and Maofa JIANG^{1,2)}

1) Key Laboratory for Ecological Metallurgy of Multimetallurgical Ores (Ministry of Education), Northeastern University, Shenyang, 110819 China. 2) School of Metallurgy, Northeastern University, Shenyang, 110819 China.

(Received on January 27, 2016; accepted on March 22, 2016)

The phase diagrams of Ti-bearing slag have fundamental guiding significance for the comprehensive utilization of Ti resources. In this article, the pseudo-melting temperatures were determined by the single hot thermocouple technique (SHTT) and high equilibrium experiments for the specified contents of 5% to 15% MgO in the CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ phase diagram system. The 1 250°C to 1 350°C liquidus lines were firstly calculated based on the thermodynamic equations in the specific primary crystal field. The phase equilibrium relationship was determined experimentally at 1 300°C using the high temperature experimental technique followed by X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDX) analysis, and the liquid Phase, liquid coexist with solid solution phase of (2CaO·MgO·2SiO₂, 2CaO·Al₂O₃·SiO₂)_{ss} were found. Therefore, the phase diagram was constructed for the specified region of the CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ system, which was consistent with the existing phase diagram except for somewhat larger liquidus area at 1 300°C. The comparison proved that the combination of liquidus temperature determination by SHTT and the high temperature experimental technique was enabled to construct the correct phase diagram for slag systems.

KEY WORDS: SHTT; Ti-bearing slag; phase diagram; high temperature equilibrium; quenching; liquidus.

1. Introduction

Titanium-bearing slag (Ti-bearing slag) produced by the blast furnace process, known as the CaO-SiO₂-MgO-Al₂O₃-TiO₂ system, contains more than 20% TiO₂¹⁾ and is considered as a valuable secondary resource. A lot of processes have been proposed for treating the slag, such as the acid leading,^{2,3)} carbide-chloride method⁴⁻⁶⁾ and the selective crystallization and phase separation method.^{7,8)} As most of the processes are operated in air atmosphere, the liquidus and phase relations of Ti-Bearing slag system in oxygen condition are necessary to facilitate improvements to the related processes. However, the phase diagram of Ti-Bearing system is difficult to study due to the high temperature and complex reactions between different components.

As the most important subsystem of Ti-bearing slag, the phase diagram of CaO-SiO₂-TiO₂ system was firstly completely investigated by DeVries *et al.*⁹⁾ and the addition of 10%–20% Al₂O₃ to CaO-SiO₂-TiO₂ system was studied by Ohno *et al.*¹⁰⁾ with a more wider content range of TiO₂ in air. It was found by Ohno *et al.*¹⁰⁾ that the liquidus temperature was decreased with the increase of TiO₂, while it was reported by Fine *et al.*¹¹⁾ that the addition of TiO₂ increases the liquidus temperature. Osborn *et al.*¹²⁾ studied the effect of additions of TiO₂ to the CaO-SiO₂-MgO-Al₂O₃ compo-

sitions on the liquidus temperatures in air atmosphere, and the results indicated that the liquidus temperatures were not greatly influenced.¹³⁾ The phase equilibrium at reducing condition was experimentally studied by Zhao *et al.*¹⁴⁾ and the melting temperature was described as a function of basicity and TiO_x concentration. However, the phase relations of the CaO-SiO₂-MgO system with the additions of Al₂O₃ and TiO₂ still remain unclear and the lack of thermodynamic information¹⁵⁻¹⁷⁾ for liquidus temperature and phase relations seriously restrict the development and application of aforementioned system.

It is well known that the basic task in phase diagram construction is the determination of the liquidus temperatures and the primary crystal phase for different compositions. In the present research, the Single Hot Thermocouple Technique (SHTT) and high temperature equilibrium technique were combined together to complete the two tasks, and the combination of this method has been proven as an accurate, reproducible and reliable method for determining the phase diagram of oxide system.¹⁸⁻²⁰⁾ Firstly, this pseudo-melting temperatures were measured by SHTT, which could achieve *in situ* observation of the melting process, and the liquidus temperatures could be calculated subsequently according to the thermodynamic equations. After the establishment of the liquidus lines, only a few number of equilibria experiments were needed to confirm the primary phase of different compositions. The method used in this research could save much time without reducing the measurement accuracy. The

* Corresponding author: E-mail: sunlf@smm.neu.edu.cn
DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-045>

investigation described here was one part of a long-term study for Ti-bearing slag system and the result from the present study could also provide important information for the optimization of the thermodynamic database.

2. Experiment

2.1. Sample Preparation

Reagent grade oxides powders of CaO (99.99 wt pct pure), SiO₂ (99.99 wt pct pure), MgO (99.99 wt pct pure), Al₂O₃ (99.99 wt pct pure) and TiO₂ (99.99 wt pct pure) were employed to synthesize the slags, which were calcined at 1 000°C for 4 h to evaporate the moisture and impurities, carefully weighted, fully mixed and pre-melted in Ar atmosphere by a vertical MoSi₂ furnace with temperature

accuracy estimated to be $\pm 2^\circ\text{C}$. The mixtures were placed in platinum crucibles which were suspended by platinum wire inside the hot zone of the furnace at 1 650°C for 2 h to completely homogenize the slag. The samples were then quenched into ice water, dried, crushed and ground under 200 mesh for further utilization. The composition of quenched slags may differ from those of the designed samples because of evaporation losses. X-Ray Fluorescopy (XRF) was then applied to analyze the compositions for comparison. The results of both are listed in **Table 1**, where the measured values showed a small deviation compared with the designed composition.

2.2. The Measurement of Pseudo-melting Temperature

The SHTT technique was employed to measure the melt-

Table 1. The designed and measured composition of CaO–SiO₂–MgO–Al₂O₃–TiO₂ slags, mass pct.

Slag NO.		$w(\text{CaO})/w(\text{SiO}_2)$	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	Total
E1	Measured	0.83	36.28	43.67	5.06	10.13	4.86	100.00
	Designed	0.90	37.80	42.20	5.00	10.00	5.00	100.00
E2	Measured	0.88	37.10	42.34	4.84	10.57	5.15	100.00
	Designed	0.80	35.56	44.44	5.00	10.00	5.00	100.00
E3	Measured	0.91	37.43	41.33	4.96	10.78	5.49	100.00
	Designed	0.81	35.89	44.11	5.00	10.00	5.00	100.00
E4	Measured	1.05	40.53	38.65	5.29	10.32	5.21	100.00
	Designed	1.00	40.00	40.00	5.00	10.00	5.00	100.00
E5	Measured	1.19	43.18	36.18	5.38	10.26	4.99	100.00
	Designed	1.20	43.64	36.36	5.00	10.00	5.00	100.00
E6	Measured	1.17	43.13	36.86	5.01	9.97	5.03	100.00
	Designed	1.18	43.30	36.70	5.00	10.00	5.00	100.00
E7	Measured	1.37	46.13	33.70	4.99	9.88	5.30	100.00
	Designed	1.34	45.81	34.19	5.00	10.00	5.00	100.00
E8	Measured	1.42	47.06	33.15	4.96	9.74	5.09	100.00
	Designed	1.36	46.10	33.90	5.00	10.00	5.00	100.00
E9	Measured	0.78	32.41	41.81	9.83	10.50	5.45	100.00
	Designed	0.74	31.99	43.01	10.00	10.00	5.00	100.00
E10	Measured	0.90	35.39	39.26	9.67	10.25	5.43	100.00
	Designed	0.86	34.64	40.36	10.00	10.00	5.00	100.00
E11	Measured	1.10	39.35	35.84	9.41	10.22	5.17	100.00
	Designed	1.03	37.98	37.02	10.00	10.00	5.00	100.00
E12	Measured	0.68	28.08	41.31	15.00	10.06	5.54	100.00
	Designed	0.65	27.67	42.33	15.00	10.00	5.00	100.00
E13	Measured	0.79	30.87	38.86	14.51	10.24	5.52	100.00
	Designed	0.77	30.45	39.55	15.00	10.00	5.00	100.00
E14	Measured	0.86	32.43	37.70	14.55	10.19	5.13	100.00
	Designed	0.85	32.16	37.84	15.00	10.00	5.00	100.00
E15	Measured	0.95	34.19	36.04	14.42	10.10	5.25	100.00
	Designed	0.91	33.42	36.58	15.00	10.00	5.00	100.00

ing temperatures of the slags in the present experiments. The principle of SHTT has been described in details^{21–23)} and is briefly summarized in this study. A B-type thermocouple (0.2-mm in diameter) was used to heat and measure the temperature simultaneously. A microscope equipped with a video camera was applied to *in-situ* observe and record the images of slag, which were sent to a computer and a video cassette recorder. The heating process was controlled by a computer program.

The melting temperature of a slag could be defined as the temperature at which the last small crystal disappeared according to Ohno *et al.*,¹⁰⁾ in consideration of the easier judgement and reproducibility of the melting temperatures, the definition of melting temperature was a little different in present work. The following method, as illustrated in **Fig. 1**, was used for the determination of the melting temperatures.

During the experiments, approximately 10 mg slag was mounted on the tip of thermocouple and rapidly heated by 5–10°C/s to a point 50–200°C below the approximate melting temperature, as shown in Fig. 1(a). As the temperature was most accurate at the tip of the thermocouple, the part of the slag surrounding the tip of the thermocouple was taken as observing object, as shown in the circular arc area in Figs. 1(a) and 1(b). It was clearly seen that the slag was completely solid in Fig. 1(a). Then, the slag was heated continuously at a very slow rate of 0.1°C/s to the temperature shown in Fig. 1(b), at which the slag close to the tip of the thermocouple firstly became liquid and transparent while the slag far away from the thermocouple tip was still solid phase, which meant the slag around the thermocouple tip had already been in the liquid state. The temperature of the state in Fig. 1(b) was found reproducible and could be taken as the melting temperature of the slag, which was called pseudo-melting temperature in this paper. With the temperature further increased, all of the slag became liquid in Fig. 1(c) due to the heat transfer. The whole melting process of the slag was recorded as a video file and the pseudo-melting temperature was then obtained.

Every measurement was performed at least three times to verify the reproducibility. The B-type thermocouple was calibrated against the pure NaF (992°C) to ensure the temperature accuracy within $\pm 1^\circ\text{C}$ at the beginning of each measurement.

2.3. Equilibration Experiments

The vertical furnace used for pre-melting was employed for the equilibrium experiments. The furnace temperature was monitored by a B-type thermocouple placed next to the samples with an overall temperature accuracy estimated to be $\pm 2^\circ\text{C}$. The platinum crucibles, holding specific oxide mixtures, were suspended by a platinum wire (0.5-mm-diameter) in the hot zone of the furnace. All samples were pre-melted before equilibration at temperature of 1650°C for 3 hours, after which the furnace temperature was cooled to the equilibration temperature, an equilibration time of 24 hours based on the experience reported by previous authors^{24–26)} was used to ensure equilibrium had been achieved. Ar (99.99 pct pure) gas was passed through the furnace during the whole experiment to avoid moisture and other potential contamination sources. The base of the furnace was removed prior to rapid quenching of the sample

Fig. 1. The judgement standard of pseudo-melting temperature by the SHTT method.

directly into ice water just below the furnace. Samples were then dried and mounted in epoxy resin and polished for analysis. X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDX) were used to identify the co-existing phase and analyze the composition of each sample.

For obtaining more accurate phase compositions, the partition of elements in each phase were examined several times in different areas of the sample, the average concentration of each phase was determined through repeated

analyses to conquer the roughness of EDX.

3. Results and Discussion

3.1. Results of Pseudo-melting Temperature

The pseudo-melting temperatures determined by SHTT are listed in **Table 2**. The results of the temperatures from T_1 to T_3 were close to each other, and the average value of T_1 , T_2 and T_3 was chosen as the final pseudo-melting temperature T .

The pseudo-melting temperatures change differently with the increase of $w(\text{CaO})/w(\text{SiO}_2)$ at 5% content of MgO , as shown in **Fig. 2**. The pseudo-melting temperatures first decreased from 1 261°C to 1 257°C when $w(\text{CaO})/w(\text{SiO}_2)$ increased from 0.83 to 0.91, and then increased to 1 409°C when $w(\text{CaO})/w(\text{SiO}_2)$ was further increased to 1.42. The reason for this phenomenon may be that the experimental points go across different primary crystal fields. Combined with the phase diagram¹²⁾ in Fig. 2, it could be found that the experimental points were found to pass through the primary crystal field of $\text{CaO} \cdot \text{SiO}_2$ and the solid solution $(2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2, 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)_{\text{ss}}$ ($(\text{C}_2\text{MS}_2, \text{C}_2\text{AS})_{\text{ss}}$) to the high temperature primary crystal field of $2\text{CaO} \cdot \text{SiO}_2$ with the increase of $w(\text{CaO})/w(\text{SiO}_2)$. Temperature change with $w(\text{CaO})/w(\text{SiO}_2)$ was found to show three different gradients in different areas, namely E1–E3, E3–E7 and E7–E8, which is corresponding to the three different primary crystal fields mentioned above.

3.2. Construction of the Liquidus Lines

The gradient change in different areas could be explained by the thermodynamic equations, which could be deduced with reference to the isothermal phase diagram in **Fig. 3**. In the primary crystal field of B, the point M located on the liquidus line represents the equilibrium of solid B with

liquid L.

When the liquid slag is taken as ideal solution, Eq. (1) could be deduced.

$$u_{B(l)} = u_{B(s)} \dots\dots\dots (1)$$

The terms $u_{B(l)}$ and $u_{B(s)}$ in Eq. (1) are the chemical potential of liquid B and solid B respectively. When pure solid oxide and pure liquid are taken as the standard states, the chemical potential of solid B and liquid B can be expressed as Eqs. (2) and (3) respectively:

$$u_{B(l)} = u_{B(l)}^\theta + RT \ln x_{B(l)} = G_{B(l)}^\theta + RT \ln x_{B(l)} \dots\dots\dots (2)$$

$$u_{B(s)} = u_{B(s)}^\theta + RT \ln x_{B(s)} = G_{B(s)}^\theta + RT \ln x_{B(s)} \dots\dots\dots (3)$$

The term R is the gas constant. The term T is the isothermal temperature. The terms $x_{B(l)}$ and $x_{B(s)}$ are the mole fraction of B in liquid and solid, respectively. The value

Fig. 2. The change of pseudo-melting temperatures with $w(\text{CaO})/w(\text{SiO}_2)$ compared with the primary crystal field in phase diagram.

Fig. 3. Schematic of iso-thermal A-B-C phase diagram at temperature of T .

Table 2. The determined pseudo-melting temperatures by SHTT for $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$ slags.

NO.	$w(\text{CaO})/w(\text{SiO}_2)$	$T_1, ^\circ\text{C}$	$T_2, ^\circ\text{C}$	$T_3, ^\circ\text{C}$	$T, ^\circ\text{C}$
E1	0.83	1 262	1 263	1 258	1 261
E2	0.88	1 260	1 258	1 260	1 259
E3	0.91	1 255	1 263	1 253	1 257
E4	1.05	1 296	1 302	1 298	1 299
E5	1.19	1 340	1 344	1 348	1 344
E6	1.31	1 359	1 362	1 361	1 361
E7	1.37	1 372	1 376	1 378	1 375
E8	1.42	1 410	1 409	1 408	1 409
E9	0.78	1 264	1 254	1 258	1 259
E10	0.9	1 296	1 298	1 297	1 297
E11	1.1	1 363	1 359	1 363	1 362
E12	0.68	1 291	1 294	1 290	1 292
E13	0.79	1 301	1 302	1 303	1 302
E14	0.86	1 327	1 332	1 328	1 329
E15	0.95	1 353	1 357	1 358	1 356

$$T = (T_1 + T_2 + T_3) / 3$$

of $x_{B(s)}$ is 1 when the pure solid oxide is taken as standard state. By Combining Eqs. (2) and (3) with Eq. (4) and Gibbs-Helmholtz equation in Eq. (5), the following Eq. (6) can be deduced:

$$\Delta G_{B(fus)}^\theta = G_{B(l)}^\theta - G_{B(s)}^\theta \quad \text{..... (4)}$$

$$\Delta G_{B(fus)}^\theta = \Delta H_{B(fus)}^\theta \left(1 - \frac{T}{T_m} \right) \quad \text{..... (5)}$$

(a) 5% MgO

(b) 10% MgO

(c) 15% MgO

Fig. 4. The fitting curve of pseudo-melting temperature with $w(\text{CaO})/w(\text{SiO}_2)$ at 5% to 15% content of MgO.

$$x_{B(l)} = \exp \left[-\frac{\Delta H_{B(fus)}^\theta}{R} \frac{1}{T} + \frac{\Delta H_{B(fus)}^\theta}{RT_m} \right] \quad \text{..... (6)}$$

The terms T_m and $\Delta H_{B(fus)}^\theta$ in Eq. (6) are the melting temperature and the standard enthalpy change for fusion of pure B respectively. The values of R , T_m and $\Delta H_{B(fus)}^\theta$ are almost constant and the term $x_{B(l)}$ represents the variables of composition, which can be simplified as x . Thus, Eq. (6) can be simplified to Eq. (7).

$$x = \exp \left(\frac{a}{T} + b \right) \quad \text{..... (7)}$$

Equation (7) can be further simplified to discuss the relationship of T with composition x , as shown in Eq. (8):

$$T = \frac{a}{\ln x - b} \quad \text{..... (8)}$$

Equation (8) can be used to fit the relationship between the temperature T and composition x in the specific primary crystal field of substance B. The notation a and b means $-\frac{\Delta H_{B(fus)}^\theta}{R}$ and $\frac{\Delta H_{B(fus)}^\theta}{RT_m}$ respectively, which are constant and can be regressed from the experimental measured pseudo-melting temperatures.

In the actual fitting process, the experimental points within the same primary crystal field are chosen. The fitting work was conducted by the following steps: first, the pseudo-melting temperature changes with $w(\text{CaO})/w(\text{SiO}_2)$ at different concentration of MgO was plotted, then Eq. (8) was adopted for the regression of the relationship of temperature and $w(\text{CaO})/w(\text{SiO}_2)$. **Figure 4** shows the fitting results for the different contents of MgO at 5%, 10% and 15% and the regressive equations could be found with the fitting in Fig. 4.

Based on the regressive equations, the composition of the 1 250°C, 1 300°C and 1 350°C liquidus lines for the CaO-SiO₂-MgO-10% Al₂O₃-5% TiO₂ system were calculated in **Table 3**. The liquidus lines were plotted with dot lines, as shown in **Fig. 5**. The liquidus lines from Osborn *et al.*¹²⁾ were plotted together as solid lines for comparison. As shown in the figure, the liquidus lines from both agreed well with each other, except that the liquidus lines from present study indicated a little expanded liquidus area.

Table 3. The calculated compositions for the 1 250°C to 1 350°C liquidus lines, mass pct.

NO.	$w(\text{CaO})/w(\text{SiO}_2)$	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	$T, ^\circ\text{C}$
C1	0.88	37.43	42.57	5.00	10.00	5.00	1 250
C2	0.75	32.26	42.74	10.00	10.00	5.00	1 250
C3	1.05	41.02	38.98	5.00	10.00	5.00	1 300
C4	0.90	35.51	39.49	10.00	10.00	5.00	1 300
C5	0.78	30.77	39.23	15.00	10.00	5.00	1 300
C6	1.24	44.34	35.66	5.00	10.00	5.00	1 350
C7	1.06	38.55	36.45	10.00	10.00	5.00	1 350
C8	0.93	33.77	36.23	15.00	10.00	5.00	1 350

3.3. Estimation of Equilibrium Phase

In order to clarify the phase relations in the CaO-SiO₂-MgO-10% Al₂O₃-5%TiO₂ system, samples E2, E5, E6, E10 and E11 were selected for equilibration at 1 300°C to detect the primary phase. The composition of the co-exist phases detected by EDS at 1 300°C are listed in **Table 4**. In **Table 4** and following figures, L stands for liquid, C₂S stands for 2CaO·SiO₂ and (C₂MS₂, C₂AS)_{ss} stands for (2CaO·MgO·2SiO₂, 2CaO·Al₂O₃·SiO₂)_{ss}.

Sample E2 was present as a single phase at 1 300°C. The composition of this single phase in **Table 4** was similar to the initial pre-melted composition of E2, which indicated that E2 was liquid at 1 300°C. On the other hand, this result was in accordance with the pseudo-melting temperature determined by SHTT in **Table 2**, in which the pseudo-melting temperature of E2 is 1 259°C. The situation of E10 was similar to E2 and the equilibrium phase was also liquid.

As for sample E6, it can be concluded from the microstructure in **Fig. 6(a)** and XRD result in **Fig. 7** that only the crystal of solid solution phase (C₂MS₂, C₂AS)_{ss} with dark gray in **Fig. 6(a)** was detected. However, the EDS results in **Table 4** suggested that the 2CaO·SiO₂ phase shown as

ellipse shape existed in sample E6. In order to confirm the equilibrium phase co-exist at 1 300°C, the EDS results were further projected on the CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ phase diagram in **Fig. 8**. The compositions of the light gray phase, pre-melt composition of E6 and solid solution phase (C₂MS₂, C₂AS)_{ss} lay in a straight line, which illustrated that the light gray phase and solid solution phase of (C₂MS₂, C₂AS)_{ss} co-existed in the equilibrium phase according to the lever rule. On the contrary, the 2CaO·SiO₂ phase was confirmed as precipitations during the cooling process due to the finite quenching speed according to the XRD and EDX results. Therefore, the equilibrium phases of sample E6 were solid solution phase ((C₂MS₂, C₂AS)_{ss}) and liquid phase, in which the light gray phase was liquid phase. It is worth mentioning that it seemed an eutectic reaction of L→(C₂MS₂, C₂AS)_{ss}+2CaO·SiO₂ occurred near this composition and near 1 300°C.

Figures 6(b) and 6(c) present the typical SEM microphotograph of Liquid-(C₂MS₂, C₂AS)_{ss} equilibrium for samples E5 and E11, the corresponding XRD results of E5 and E11 from **Fig. 7** and the composition in **Table 4** indicated that the dark gray phase in **Figs. 6(b)** and **6(c)** was the solid solution phase of (C₂MS₂, C₂AS)_{ss}, whereas the light gray phase was the liquid phase.

The compositions of liquid phase are compared with the calculated 1 300°C liquidus line on the pseudo-ternary CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ phase diagram in **Fig. 9**. As can be seen, the liquidus composition of E11 located on the calculated 1 300°C liquidus line, which means the results of high-temperature equilibria experiments are well in accordance with the liquidus line calculated based on the pseudo-melting temperatures measured by SHTT. Furthermore, coupled with the E5 and E6 liquid compositions projected on **Fig. 9**, the calculated 1 300°C liquidus line could be extended to lower MgO area, as shown with the dash dot line. The 1 300°C liquidus line from Osborn *et al.*¹²⁾ was plotted as solid line in the same figure for comparison, the tendency of both 1 300°C liquidus lines change with composition is the same and the locations of the 1 300°C liquidus lines are close to each other, while the 1 300°C liquidus line from present research shown a larger liquid area.

Fig. 5. Comparison of the liquidus lines between present work and Osborn *et al.*¹²⁾

Table 4. Experimental determined phase compositions of CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ system at 1 300°C.

Sample	Contrast in the SEM microphotograph	Phase	Composition, mass pct				
			CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂
E2	gray	L	35.69	45.32	5.07	9.00	4.92
E5	light gray	L	46.16	37.60	3.33	6.85	6.07
	dark gray	(C ₂ MS ₂ , C ₂ AS) _{ss}	42.96	37.72	8.15	11.17	—
E6	light gray	L	49.58	41.30	1.62	7.50	—
	dark gray	(C ₂ MS ₂ , C ₂ AS) _{ss}	42.17	38.10	7.42	12.31	—
	ellipse shape	C ₂ S	65.72	34.28	—	—	—
E10	gray	L	35.54	39.73	9.69	9.89	5.15
E11	light gray	L	32.82	36.07	8.81	11.97	10.34
	dark gray	(C ₂ MS ₂ , C ₂ AS) _{ss}	40.38	39.83	10.73	9.06	—

L=Liquid; C₂S=2CaO·SiO₂; (C₂MS₂, C₂AS)_{ss}=(2CaO·MgO·2SiO₂, 2CaO·Al₂O₃·SiO₂)_{ss}.

(a) Sample E6

(b) Sample E5

(c) Sample E11

Fig. 6. Microstructure of equilibria phases under 1300°C.

3.4. Presentation of the Phase Diagram

Coupled with the liquidus lines in Fig. 5 and the confirmed equilibrium phases at 1300°C, the phase diagram at specific area for the CaO-SiO₂-MgO-10% Al₂O₃-5% TiO₂ system was constructed, which was compared with the results from Osborn *et al.*¹²⁾ in Fig. 10. As can be seen, most of the experimental points were located within the (C₂MS₂, C₂AS)_{ss} primary crystal field. The solid dots were the points selected for the equilibrium experiments at

Fig. 7. XRD results of equilibria samples E5, E6 and E11 at 1300°C.

 Fig. 8. Projection of EDS results on CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ phase diagram for sample E6.

Fig. 9. Comparison of experimental liquid composition with liquidus line for samples E5, E6 and E11 at 1300°C.

Fig. 10. Comparison between the present experimental results with the phase diagram suggested by Osborn *et al.*¹²⁾

1300°C. The single phase of liquid were determined for samples E2 and E10, and two phase equilibrium of liquid with $(C_2MS_2, C_2AS)_{ss}$ were confirmed for samples E5, E6 and E11. These findings were consistent with the phases suggested by Osborn *et al.*¹²⁾ The consistent comparison results indicate that the combination of SHTT and the high temperature equilibrium technique was enabled to obtain the correct phase diagram for the slag system.

4. Conclusion

The coupled SHTT/high temperature equilibrium experimental approach has been developed and applied to investigate the pseudo-melting temperatures and the phase relations for 5%–15% MgO in the CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ system. The 1250°C to 1350°C liquidus lines were firstly calculated according to thermodynamic equations in the specific primary crystal field. The liquid phase co-exist with $(C_2MS_2, C_2AS)_{ss}$ solid solution phase was confirmed. Based on the experimental results, a phase diagram was constructed for the specified region of the CaO-SiO₂-MgO-10%Al₂O₃-5%TiO₂ system. The liquid region according to the present work should be somewhat extended when compared with the work by Osborn *et al.*¹²⁾ However, the results from the present study generally agree well with the phase diagram suggested by Osborn *et al.*¹²⁾ It is worth

mentioning that the experimental work completed on this system indicated that the coupled SHTT and high temperature equilibrium technique could be used to construct the correct phase diagram for the slag system.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (Nos. 51374059, 51104039 and 51304042), Scientific Research Fund of Liaoning Provincial Education Department (No. L2013114), Programs of Liaoning province for Science and Technology Development (No. 2012221013), the Fundamental Research Funds for the Central Universities of China (N130602002).

REFERENCES

- 1) W. Zhang, L. Zhang, J. H. Zhang and N. X. Feng: *Ind. Eng. Chem. Res.*, **51** (2012), 12294.
- 2) X. H. Liu and Z. T. Sui: *China J. Nonferr. Met.*, **12** (2002), 1281.
- 3) M. H. Wang, X. H. Du and Z. T. Sui: *Multipurp. Util. Miner. Resour.*, **4** (2000), 5.
- 4) I. Brain and W. Schuler: *Metall. Mater. Trans. B*, **11B** (1980), 199.
- 5) Y. Peng: *Titanium Ind. Prog.*, **22** (2005), 45.
- 6) Y. M. Wang, R. F. Liu, R. H. Zhou, B. S. Shao, Q. S. Wei, Z. F. Yuan and C. Xu: *Comput. Appl. Chem.*, **23** (2006), 263.
- 7) X. D. Wang, Y. W. Mao, X. Y. Liu and Y. K. Zhu: *J. Iron Steel Res.*, **3** (1990), 1.
- 8) Y. Q. Sun, J. Li, X. D. Wang and Z. T. Zhang: *Metall. Mater. Trans. B*, **45B** (2014), 1446.
- 9) R. C. DeVries, R. Roy and E. F. Osborn: *Am. Ceram. Soc.*, **38** (1955), 15.
- 10) A. Ohno and H. U. Ross: *Can. Metall. Q.*, **3** (1963), 243.
- 11) H. A. Fine and S. Arac: *Ironmaking Steelmaking*, **4** (1980), 160.
- 12) E. F. Osborn and K. H. Gee: *Bull. Earth Miner. Sci. Exp., Stn.*, **85** (1969), 57.
- 13) Slag Atlas, ed. by VDEh, Verlag Stahleisen GmbH, Düsseldorf, (1995), 39.
- 14) B. J. Zhao, J. Eugene and P. C. Hayes: 2009 CSM Annual Meeting Proc., Metallurgical Industry Press, Beijing, (2009), 438.
- 15) H. M. Liu, H. Du and Z. P. Yang: *Acta Metall. Sin.*, **28** (1992), B45.
- 16) S. M. Jung and R. J. Fruehan: *ISIJ Int.*, **41** (2001), 1447.
- 17) Y. Morizane, B. Ozturk and R. J. Fruehan: *Metall. Mater. Trans. B*, **30** (1999), 29.
- 18) J. J. Shi, L. F. Sun, B. Zhang, X. Q. Liu, J. Y. Qiu, Z. Y. Wang and M. F. Jiang: *Metall. Mater. Trans. B*, **47** (2015), 425.
- 19) J. J. Shi, L. F. Sun, X. Q. Liu, Z. Y. Wang, J. Y. Qiu and M. F. Jiang: *J. Cent. South Univ. (Sci. Tech.)*, (2015), accepted.
- 20) L. F. Sun, J. J. Shi, B. Zhang, J. Y. Qiu, Z. Y. Wang and M. F. Jiang: *J. Cent. South Univ.*, (2016), accepted.
- 21) Y. Kashiwaya, C. E. Cicutti, A. W. Cramb and K. Ishii: *ISIJ Int.*, **38** (1998), 348.
- 22) J. Li, Z. T. Zhang, L. L. Liu, W. L. Wang and X. D. Wang: *ISIJ Int.*, **53** (2013), 1696.
- 23) D. Xiao, W. L. Wang and B. X. Lu: *Metall. Mater. Trans. B*, **46** (2015), 873.
- 24) H. M. Henao, F. Kongoli and K. Itagaki: *Mater. Trans.*, **46** (2005), 812.
- 25) Y. B. Kang and H. G. Lee: *ISIJ Int.*, **45** (2005), 1552.
- 26) H. M. Henao, C. Pizarro, J. K. Front, A. Moyano, P. C. Hayes and E. Jak: *Metall. Mater. Trans. B*, **46** (2010), 1186.