Effect of Al_2O_3 Addition on the Phase Equilibria Relations of CaO-SiO_2 -5 wt%MgO- Al_2O_3 - TiO_2 System Relevant to Ti-bearing Blast Furnace Slag

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The influence of Al_2O_3 addition up to 30 wt% on equilibria phase relations of Ti-bearing slag system with $w(\text{CaO})/w(\text{SiO}_2)$ of 1.00 was investigated at 1 300°C and 1 400°C by classical high temperature thermodynamic equilibria technique followed by XRD (X-Ray diffraction) and SEM-EDX (Scanning Electron Microscope and Energy Dispersive X-ray Fluorescence scope) analysis. Experimental results indicated that with the increase of Al_2O_3 addition the equilibria solid phases gradually change from melilite solid solution and perovskite to Al-Ti diopside solid solution, spinel, and pseudobrookite solid solution. Moreover, comparisons with the predictions by Factsage 7.2 revealed that the calculated equilibria phase relations were only well agreed with experimental results below 20 wt% Al_2O_3 and TiO_2 , while great deviations presented when Al_2O_3 content higher than 20 wt%. Based on experimental and calculated results, the 1 300°C and 1 400°C liquidus lines as well as the predicted primary crystal phase boundary lines were constructed for specific composition range of CaO-SiO_2 -5wt%MgO- Al_2O_3 - TiO_2 system.

KEY WORDS: phase diagram; equilibrium; Ti-bearing slag; Factsage; liquidus; Al_2O_3 addition.

1. Introduction

It is well known that vanadium-titanium magnetite is widely distributed all over the world including South Africa, Australia, Russia, and China.¹⁾ Until now, most of the magnetite ore is disposed by high blast furnace smelting process, after which most of the iron and vanadium compounds are reduced into hot metal for the following utilization in the subsequent processes,^{2,3)} while most of titanium components are transferred into slag phase, which is called Ti-bearing slag. Ti-bearing slag has been considered as a valuable secondary resource due to its TiO_2 content is higher than 20 wt%.²⁾ Unfortunately, Ti-bearing slag is difficult to be recovered mainly due to the reason that Ti element is finely dispersed in many different kinds of Ti-containing phases with complex compositions including perovskite, Ti-rich diopside, and anosovite phases.⁴⁾ As a result, several processes have been developed to explore effective utilization of Ti-bearing slag resources, such as alkali roasting leaching,⁵⁾ microwave heating,⁶⁾ and selective crystallization and phase separation (SCPS) technique,^{7,8)} among which SCPS technique has been regarded as a competitive method to dispose Ti-bearing slag and has been extensively studied over the last decades.

The principle of SCPS technique is to enrich the Ti ele-

ment into a certain Ti-rich phase, and to make the selected phase fully grow by adjusting compositions, temperatures, or the cooling rates, then followed by further separation through gravity or flotation to obtain the Ti-enriched phase. The competitive alternative Ti-rich phases are rutile,^{8–10)} anosovite,¹¹⁾ and perovskite¹²⁾ phase, as the theoretical TiO_2 content are 100 wt%, more than 70 wt%,¹³⁾ and 58.82 wt% for the three phases, respectively. However, the chemical composition of Ti-bearing slag changes frequently due to the different source of vanadium-titanium magnetite ore and the parameters with different smelting process. Therefore, the first step of SCPS process is to adjust the composition of Ti-bearing slag to ensure the formation of target Ti-rich phases. Based on this point of view, a lot of studies have been done to achieve this goal by different additives, and it was found that the addition of CaO, MnO, and Fe_2O_3 ^{14,15)} were favorable for the precipitation of perovskite phase, while the rutile formation was prompted by the addition of P_2O_5 and B_2O_3 ,^{8,10)} and the addition of B_2O_3 was also beneficial for the concentration of anosovite phase.¹³⁾ The precipitation behaviors of these Ti-rich phases have been extensively studied from the perspective of dynamic methods, i.e. the cooling rate, crystallization, time-temperature-transformation (TTT) curves, viscosity, however, the thermodynamic studies by constructing the phase diagrams, which could be served as a guideline for adjusting the composition of Ti-bearing slag, has rarely been investigated.

Most of the phase equilibrium investigations for Ti-

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bearing slag are focus on the subsystems including CaO–SiO₂–TiO₂,¹⁶⁾ CaO–SiO₂–TiO₂–Al₂O₃,^{17,18)} CaO–SiO₂–MgO–Al₂O₃,^{19,20)} etc. The first systematic experimental study for CaO–SiO₂–MgO–Al₂O₃–TiO₂ system was completed by Osborn *et al.*²¹⁾ at the year of 1969 to discuss the “gumminess” phenomenon caused by the TiO₂, the results from Osborn *et al.*²¹⁾ were plotted on pseudo-ternary phase diagram with constant Al₂O₃ and TiO₂ contents, and it was found that the substitution of TiO₂ for Al₂O₃ has little influence on the liquidus temperatures. Inspired by the SCPS technique with anosovite phase as the Ti-rich phase, Zhen Wang *et al.*^{18,22)} conducted the phase equilibria study for the TiO₂ rich part of CaO–SiO₂–TiO₂–10wt%Al₂O₃ system¹⁸⁾ and CaO–SiO₂–TiO₂–10wt%Al₂O₃–5wt%MgO system²²⁾ to explore the primary crystal field of anosovite phase, however, the primary phase region of anosovite phase was not found within the composition and temperature ranges studied by Zhen Wang *et al.*^{18,22)} Zhao *et al.*²³⁾ investigated the phase equilibria relationship and liquidus temperatures of CaO–SiO₂–MgO–Al₂O₃–TiO₂ system under reducing atmosphere, and the results were mainly presented with fixed $w(\text{MgO})/w(\text{CaO})$ and $w(\text{Al}_2\text{O}_3)/w(\text{SiO}_2)$ ratio, and it was found that it was possible to recover TiO₂ in the form of pseudobrookite phase (a solid solution of MgO·2TiO₂, Al₂O₃·TiO₂, and Ti₂O₃·TiO₂). Nevertheless, the phase equilibria studies aimed at Ti-bearing slag system are still not enough and the phase equilibria information for Ti-bearing slag is still far from sufficient for the comprehensive utilization of Ti resources and for the development of related processes.

As point out and studied by Zhongmin Li *et al.*²⁴⁾ that the precipitation of Ti-rich phases could be obviously influenced by the addition of Al₂O₃, therefore, the phase equilibria relations for CaO–SiO₂–MgO–Al₂O₃–TiO₂ system with the addition of Al₂O₃ up to 30 wt% will be studied in present work, which is also a part of continuous researches aim at systematic studying the thermodynamic properties for Ti-bearing slag conducted during the past few years.^{25–28,35)} The results from present work will not only provide direct thermodynamic data for the comprehensive recovery of Ti-bearing slag and the high blast furnace smelting process

of magnetite ore, but also can be served as important references for the optimization and development of Ti-containing thermodynamic database, *i.e.* Factsage, and HSC software, etc.

2. Experimental

2.1. Sample Composition

In order to clarify the transformation of equilibria phase relations related to practical composition of Ti-bearing slag system, the compositions of the experimental samples were designed mainly basing on the typical composition^{29,30)} of Ti-bearing slag (**Table 1**) generated from the high blast furnace smelting process. During last few years, the equilibria phase relations at constant Al₂O₃ content of 10 wt%,^{28,35)} 20 wt%²⁶⁾ and 30 wt%²⁷⁾ with varying $w(\text{CaO})/w(\text{SiO}_2)$ were continuous investigated by present authors,²⁵⁾ which lays the foundation of studying equilibria phase relations for Ti-bearing slag system and makes it possible to carry out the analysis of the influence of Al₂O₃ addition on the equilibria phase relations for CaO–SiO₂–MgO–Al₂O₃–TiO₂ system. Therefore, samples from previous studies^{25–28,35)} with fixed $w(\text{CaO})/w(\text{SiO}_2)$ of 1.00 and different Al₂O₃ content up to 30 wt% were selected to analysis the influence of Al₂O₃ addition on the equilibria phase relations, and the projections of the sample compositions in tetrahedron and pseudo-ternary phase diagrams were shown in **Figs. 1(a)** and **1(b)**, while the specific compositions were shown in **Table 2**, accordingly.

2.2. Pre-melting Experiment and High Temperature Equilibria Experiment

The experimental processes have been explained in detail in previous works^{25–28,35)} and will be simply described in this section. Generally, the experimental process could be

Table 1. Typical composition of Ti-bearing slag, (wt%).

$w(\text{CaO})/w(\text{SiO}_2)$	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃
0.8–1.2	20–30	22–26	4–9	10–15	20–30	1–4

Fig. 1. (a) Tetrahedron presentation of Ti-bearing slag with $w(\text{CaO})/w(\text{SiO}_2) = 1.00$, and (b) pseudo-ternary projection of the sample compositions. (Online version in color.)

divided into two parts, *i.e.* pre-melting experiment and high temperature equilibria experiment.

Pre-melting experiments were carried out to obtain homogeneous molten slag by fully mixing the high purity of CaO (99.99 wt%), SiO₂ (99.99 wt%), MgO (99.99 wt%), Al₂O₃ (99.99 wt%) and TiO₂ (99.99 wt%) oxide powders from Sinopharm Chemical Reagent Co., Ltd, China, and the pre-melting experiments were conducted in a MoSi₂ furnace (GCL-01, Northeastern University, temperature accuracy calibrated to be $\pm 2^\circ\text{C}$) under Ar atmosphere at 1 650°C for 2 h, followed by quenching the samples into ice water. The successful pre-melting experiments were examined by X-Ray Powder Diffraction (XRD, X'Pert Pro, Panalytical B V, Intensities were collected by 2 θ scanning, the generator voltage and tube current were 40 kV and 40 mA, respectively, the scanning ranges from 10° to 80° was measured at a step of 0.02°) with Cu K α radiation and Scanning Electron Microscope (SEM, JXA-8530F, JEOL), and only the pre-

melting results shown as uniform phase in Fig. 2(a) and glassy phase in Fig. 2(b) could be adopted for the following equilibrium experiments.

After pre-melting experiments, the classic high temperature thermodynamic equilibria technique followed by rapid quenching was employed to investigate the phase equilibria for Ti-bearing slag system. The platinum crucible containing the pre-melted sample was suspended by platinum wire in the even temperature zone of the vertical tube furnace, which was also used for the pre-melting experiments. The sample was re-heated to 1 650°C for 2 h to obtain the homogeneous molten melt again, thereafter, the temperature was cooled down to the equilibrium temperature (1 300°C or 1 400°C) and preserved for a long period until the equilibrium reached. Preliminary experiments were designed to compare the equilibrium results after different holding times (12, 18, 24, 36 and 48 hours), and the results indicated that 24 hours was sufficient for the equilibrium, and 24 h was also proved to be enough for the reach of equilibrium according to other similar studies.²²⁾ Therefore, all of the samples in present research will be preserved for at least 24 h to ensure the equilibrium state had been reached. Afterwards, the sample was rapid quenched to room temperature

Table 2. Designed composition of the samples for Ti-bearing slag, (wt%).

Sample No.	w(CaO)/w(SiO ₂)	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂
D1	1.00	40.00	40.00	5.00	10.00	5.00
D2	1.00	35.00	35.00	5.00	10.00	15.00
D3	1.00	32.50	32.50	5.00	10.00	20.00
D4	1.00	35.00	35.00	5.00	20.00	5.00
D5	1.00	32.50	32.50	5.00	20.00	10.00
D6	1.00	27.50	27.50	5.00	20.00	20.00
D7	1.00	25.00	25.00	5.00	20.00	25.00
D8	1.00	25.00	25.00	5.00	30.00	15.00
D9	1.00	22.50	22.50	5.00	30.00	20.00
D10	1.00	20.00	20.00	5.00	30.00	25.00

Fig. 2. Homogeneous molten slag obtained by pre-melting experiments, (a) SEM, (b) XRD.

Fig. 3. Microstructure of the equilibria phases at 1 400°C analyzed by SEM. (a) D1 (b) D3 (c) D6 (d) D8 (e) D9 (f) D10.

by directly dropping the crucible into ice water to keep the equilibrium phase assembly and compositions.

The quenched samples were then dried, ground to powder, or embedded in epoxy resin and polished for further analysis. Phase assembly was detected by XRD analysis, and the parameters were the same used for pre-melting experiments. The microstructures and compositions of the equilibria phases were measured by SEM analysis under BSE mode. The EDX measurement conditions were as follows: a beam current of 15 nA, an accelerating voltage of electron beam was 20 kV. CaSiO_3 , MgO , Al_2O_3 and TiO_2 were used as standard to analyze CaO , SiO_2 , MgO , Al_2O_3 and TiO_2 , respectively. The ZAF correction method was used to calculate the composition of CaO , SiO_2 , MgO , Al_2O_3 and TiO_2 . Six analysis points were randomly chosen for each phase in the sample for accuracy.

3. Results and Discussion

With the purpose of clarify the influence of Al_2O_3 addition on the equilibria phases relations for CaO – SiO_2 – MgO – Al_2O_3 – TiO_2 system, the high temperature equilibrium experiments have been conducted at 1 300°C and 1 400°C, the microstructures of the equilibrium phases are presented in **Fig. 3** (for 1 400°C) and **Fig. 5** (for 1 300°C), and the XRD patterns of the equilibria phases are shown in **Fig. 4** (for 1 400°C) and **Fig. 6** (for 1 300°C), while the compositions of the equilibria phases are listed in **Table 3** (for 1 400°C) and **Table 4** (for 1 300°C), respectively. In the following parts, L stands for liquid, $(\text{C}_2\text{MS}_2, \text{C}_2\text{AS})_{\text{ss}}$ stands for solid solution phase of $(2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2, 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)_{\text{ss}}$, $(\text{MT}_2, \text{AT})_{\text{ss}}$ stands for pseudobrookite solid solution phase of $(\text{MgO} \cdot 2\text{TiO}_2, \text{Al}_2\text{O}_3 \cdot \text{TiO}_2)_{\text{ss}}$.

3.1. Influence of Al_2O_3 Addition on Equilibria Phase Relations at 1 400°C

It is easy to judge from Figs. 3(a) and 4(a) that there is no crystal phase for sample D1 with 10 wt% Al_2O_3 , therefore, sample D1 could be estimated as single liquid phase at 1 400°C, similarly, sample D5 at lower TiO_2 content area with 20 wt% Al_2O_3 is also confirmed as single liquid phase and its liquid composition could be found in Table 3. While when TiO_2 content increased to sample D3 with 20 wt% TiO_2 and 10 wt% Al_2O_3 , perovskite phase of $\text{CaO} \cdot \text{TiO}_2$ was found to be coexisting with liquid phase, from the detected information in Figs. 3(b), 4(b) and Table 3, it can be confirmed that the white dendritic phase is $\text{CaO} \cdot \text{TiO}_2$ phase, while the matrix gray phase is the coexisting liquid phase. When the Al_2O_3 content was further increased to 20 wt%

Fig. 4. XRD patterns of the equilibria phases at 1 400°C analyzed by XRD.

Fig. 5. Microstructure of the equilibria phases at 1 300°C analyzed by SEM. (a) D1 (b) D2 (c) D4 (d) D6.

Al_2O_3 for samples D6 and D7 with higher TiO_2 content, it could be found from Figs. 3(c) and 4(c) that the equilibrium phase coexisting with liquid phase change from $\text{CaO}\cdot\text{TiO}_2$ phase to Al–Ti diopside phase with the general formula of $\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$, as can be seen from Fig. 3(c) that the Al–Ti diopside phase is characterized as leaf shape with dark gray phase, while the liquid phase is coexisting as light gray phase. The Al–Ti diopside solid solution phase is one of the most common phases presented in Ti-bearing blast furnace slag system and is characterized by the high solubility of Al_2O_3 and TiO_2 as listed in Table 3.^{31,32)}

The experimental results become more complicated when Al_2O_3 content continue increased to 30 wt%. As can be seen

from the microstructure in Fig. 3(d) and the XRD patterns in Fig. 4(d) for sample D8, it could be conclude that two solid phases of $\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$ and $\text{MgO}\cdot\text{Al}_2\text{O}_3$ are coexisting with liquid phase, and the dark polygon phase is $\text{MgO}\cdot\text{Al}_2\text{O}_3$, the dark gray phase is $\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$, while the light gray phase is the coexisting liquid phase, from the equilibria phase relation of sample D8 it is believed that the primary crystal phase fields of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ phase and $\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$ phase are adjacent with each other.

While when TiO_2 content keep increasing to a higher level for sample D10 at 30 wt% Al_2O_3 , another solid phase

Fig. 6. XRD patterns of the equilibria phases at 1300°C analyzed by XRD.

Table 4. Compositions of equilibria phases for $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$ system at 1300°C.

No.	contrast	Equilibria phases	Compositions, wt%				
			CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂
D1	gray	L	40.67	40.38	4.64	9.19	5.13
D2	gray	L	34.49	39.90	5.21	9.20	11.19
	white dendric	$\text{CaO}\cdot\text{TiO}_2$	39.94				60.06
D4	dark gray	L	34.64	37.91	4.04	16.94	6.46
	light gray	$(\text{C}_2\text{MS}_2, \text{C}_2\text{AS})_{\text{ss}}$	35.16	26.05		38.79	
D5	gray	L	32.90	35.09	4.68	19.21	8.12
	white dendric	$\text{CaO}\cdot\text{TiO}_2$	41.13				58.87
D6	light gray	L	26.94	38.16	5.39	20.21	9.30
	dark gray	$\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$	25.50	28.30	5.51	22.72	17.97
	white dendric	$\text{CaO}\cdot\text{TiO}_2$	41.07				58.93

Table 3. Compositions of equilibria phases for $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$ system at 1400°C.

No.	Contrast	Equilibria phases	Compositions, wt%				
			CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂
D1	gray	L	40.94	40.75	4.38	8.86	5.07
D3	gray	L	34.05	33.92	4.89	10.27	16.87
	white dendric	$\text{CaO}\cdot\text{TiO}_2$	41.86				58.14
D5	gray	L	34.63	31.25	5.23	19.37	9.52
D6	light gray	L	28.61	28.93	4.64	18.87	18.95
	dark gray	$\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$	25.60	28.35	5.53	19.49	21.03
D7	light gray	L	25.31	27.18	4.48	20.07	22.96
	dark gray	$\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$	23.62	26.20	5.87	21.10	23.21
D8	light gray	L	22.65	31.03	4.21	27.76	14.35
	black polygon	$\text{MgO}\cdot\text{Al}_2\text{O}_3$			29.29	70.71	
	dark gray	$\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$	23.62	30.43	4.47	27.29	14.18
D9	light gray	L	22.56	28.90	4.03	27.30	17.21
	black polygon	$\text{MgO}\cdot\text{Al}_2\text{O}_3$			28.92	71.08	
	dark gray	$\text{Ca}(\text{Ti, Mg, Al})(\text{Si, Al})_2\text{O}_6$	23.49	28.39	3.77	27.15	17.20
	white strip	$(\text{MT}_2, \text{AT})_{\text{ss}}$			2.19	7.47	90.34
D10	light gray	L	23.06	31.19	3.03	26.99	15.72
	black polygon	$\text{MgO}\cdot\text{Al}_2\text{O}_3$			30.18	69.82	
	white strip	$(\text{MT}_2, \text{AT})_{\text{ss}}$			3.34	9.72	86.94

known as pseudobrookite solid solution phase with the formula of $(\text{MT}_2, \text{AT})_{\text{ss}}$ is found to replace $\text{Ca}(\text{Ti}, \text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ phase to equilibrated with $\text{MgO} \cdot \text{Al}_2\text{O}_3$ phase and liquid phase, which could be proven by the microstructure in Fig. 3(f) and XRD patterns in Fig. 4(f), $(\text{MT}_2, \text{AT})_{\text{ss}}$ phase is characterized with white strip shape and is also a common phase frequently appeared in Ti-bearing blast furnace slag,⁷⁾ the equilibria phase relations for sample D10 indicate that the primary crystal phase field of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ phase is also

adjacent with the primary crystal field of $(\text{MT}_2, \text{AT})_{\text{ss}}$ phase. Based on the same method mentioned above, it could be determined with reference to Figs. 3(e) and 4(e) that sample D9 is equilibrated with three solid phases of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $\text{Ca}(\text{Ti}, \text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$, and $(\text{MT}_2, \text{AT})_{\text{ss}}$ coexisting with liquid phase, the microstructure of the equilibria phases are the same with the results above, and the equilibria compositions are shown in Table 3.

Table 5. Comparisons of experimental results with Factsage calculations.

No	$w(\text{TiO}_2)$	$w(\text{Al}_2\text{O}_3)$	Equilibrium phases at 1 300°C			Equilibrium phases 1 400°C		
			Measured	Calculated equilibrium phases and phase ratios (wt%)		Measured	Calculated equilibrium phases and phase ratios (wt%)	
D1	5	10	L	L	93.08	L	L	100
				Melilite	5.99			
				$\text{CaO} \cdot \text{TiO}_2$	0.93			
D2	15	10	L	L	84.79		L	93.55
			$\text{CaO} \cdot \text{TiO}_2$	$\text{CaO} \cdot \text{TiO}_2$	15.21		$\text{CaO} \cdot \text{TiO}_2$	6.45
D3	20	10		L	79.11	L	L	90.02
				$\text{CaO} \cdot \text{TiO}_2$	20.89	$\text{CaO} \cdot \text{TiO}_2$	$\text{CaO} \cdot \text{TiO}_2$	9.98
D4	5	20	L	L	72.50		L	100
			Melilite	Melilite	26.89			
				$\text{CaO} \cdot \text{TiO}_2$	0.61			
D5	10	20	L	L	83.19		L	100
			$\text{CaO} \cdot \text{TiO}_2$	$\text{CaO} \cdot \text{TiO}_2$	6.71			
				Melilite	10.11			
D6	20	20	L	L	69.90	L	L	99.59
			$\text{CaO} \cdot \text{TiO}_2$	$\text{CaO} \cdot \text{TiO}_2$	18.33	Diopside	$\text{CaO} \cdot \text{TiO}_2$	0.41
			Diopside	Ti-spinel	2.73			
				$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	9.04			
D7	25	20		L	68.85	L	L	100
				Ti-spinel	2.46	Diopside		
				$\text{CaO} \cdot \text{TiO}_2$	16.73			
				$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	11.96			
D8	15	30		L	36.24	L	L	92.91
				Ti-spinel	10.53	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	$\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$	7.09
				$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	28.92	Diopside		
				$\text{CaO} \cdot \text{TiO}_2$	20.15			
				$\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$	4.16			
D9	20	30		L	15.35	L	L	92.51
				Ti-spinel	14.50	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	$\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$	7.49
				$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	44.85	Diopside		
				$\text{CaO} \cdot \text{TiO}_2$	24.97	Pseudobrookite		
				$\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$	0.33			
D10	25	30		L	58.46	L	L	92.57
				Ti-spinel	3.88	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	$\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$	7.43
				$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	18.74	Pseudobrookite		
				$\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$	10.03			
				$\text{CaO} \cdot \text{TiO}_2$	8.91			

3.2. Influence of Al_2O_3 Addition on Equilibria Phase Relations at 1 300°C

Figures 5(a) and 6(a) give the equilibria results for sample D1 with 10 wt% Al_2O_3 at 1 300°C, it could be found that the equilibrium phase is the same for sample D1 at 1 400°C, which is also a single liquid phase. While when the TiO_2 content increased to sample D2 with 10 wt% Al_2O_3 , the dendritic shape phase of $\text{CaO} \cdot \text{TiO}_2$ precipitated to coexisting with liquid phase, as shown in Figs. 5(b) and 6(b). With further increase of Al_2O_3 to 20 wt% at lower TiO_2 content area, a two-phase coexisting result is detected for sample D4 as melilite solid solution phase of $(\text{C}_2\text{MS}_2, \text{C}_2\text{AS})_{\text{ss}}$ coexisting with liquid phase, as presented in Figs. 5(c) and 6(c), the dark gray polygon phase is $(\text{C}_2\text{MS}_2, \text{C}_2\text{AS})_{\text{ss}}$, while the light gray phase is the equilibrium liquid phase. While for sample D6, it could be concluded from the comparisons from Figs. 5(d) and 6(d) with 3(c) and 4(c) that the two-phase coexisting at 1 400°C is transformed as three-phase coexisting at 1 300°C, which indicates that with the decreasing of the temperature, $\text{CaO} \cdot \text{TiO}_2$ phase starts to precipitate to coexisting with $\text{Ca}(\text{Ti}, \text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ phase and liquid phase, and it is also believed that the primary crystal phase fields of $\text{Ca}(\text{Ti}, \text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ phase and $\text{CaO} \cdot \text{TiO}_2$ phase are also adjacent with each other.

3.3. Comparison of Experimental Equilibria Results with Predictions by Factsage

Factsage software is a powerful thermodynamic tool which has been widely used in pyro-metallurgy, hydro-metallurgy, electrometallurgy, ceramics, and glass technology, etc., especially in the prediction of high temperature phase equilibrium for multi-component systems.^{33,34} Therefore, the equilibria results were calculated by Factsage 7.2 for experimental compositions to compare with the experimental results in this part, which is shown in Table 5, the proportions of the equilibria phases are also calculated and listed accordingly.

It could be concluded from the comparisons that the predicted equilibria phases are well accordance with the experimental results within lower TiO_2 and Al_2O_3 contents area, the equilibria phases are the same for sample D1 at 1 400°C, D2 at 1 300°C, and D3 at 1 400°C, while for the equilibria phases of sample D1 at 1 300°C, D4 at 1 300°C and D5 at 1 300°C, the calculated results are also quite close to the experimental results, even though another solid phases presented, the ratio is relatively small, which can be read from Table 5 that only 0.93% and 0.61% $\text{CaO} \cdot \text{TiO}_2$ phase is found to be equilibrated for sample D1 at 1 300°C and D4 at 1 300°C, respectively.

However, significant discrepancies could be observed for samples with higher TiO_2 content of 20 wt% and Al_2O_3 content of 20 wt%, as can be seen, phases of Ti-spinel, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, $\text{CaO} \cdot 2\text{MgO} \cdot 8\text{Al}_2\text{O}_3$ are calculated to be the equilibria phases, while the experimental found phases of diopside solid solution, pseudobrookite solid solution and $\text{MgO} \cdot \text{Al}_2\text{O}_3$ are not included in the thermodynamic database of Factsage 7.2. The large deviations were also found by Shuai Wang *et al.*²⁾ between the predictions and experimental results, and the inconsistent calculated results are mainly lie in $\text{MgO} \cdot \text{Al}_2\text{O}_3$, melilite and M_3O_5 primary crystal phase field.

3.4. Phase Diagram of $\text{CaO-SiO}_2\text{-5wt}\%\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ System with $w(\text{CaO})/w(\text{SiO}_2)$ of 1.00

Based on the discussions above and calculated equilibria information by Factsage 7.2, the phase diagram for $\text{CaO-SiO}_2\text{-5wt}\%\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ system within specific composition range is constructed in Fig. 7. In Fig. 7, the solid lines are the 1 300°C and 1 400°C liquidus lines from experimental results, the dash lines are the predicted primary crystal phase boundary lines from present work, and the short dot lines are the 1 300°C and 1 400°C liquidus lines predicted by Factsage 7.2, while the short dash lines are the calculated phase boundary lines by Factsage 7.2.

Fig. 7. Phase diagram for the specific compositions range relevant to Ti-bearing slag system, wt%. (Online version in color.)

The change tendency of the primary phase and liquidus temperatures could be concluded from Fig. 7 as follows. In the lower Al_2O_3 and TiO_2 content area, the primary crystal phase is melilite solid solution phase of $(\text{C}_2\text{MS}_2, \text{C}_2\text{AS})_{\text{ss}}$, while it changes as perovskite phase of $\text{CaO} \cdot \text{TiO}_2$ with the increase of TiO_2 content. Meanwhile, the dominated phase becomes as Al–Ti diopside solid solution phase when Al_2O_3 content increased to about 20 wt%, with further increase of Al_2O_3 content, pseudobrookite solid solution phase of $(\text{MT}_2, \text{AT})_{\text{ss}}$ and $\text{MgO} \cdot \text{Al}_2\text{O}_3$ phase start to emerge as the dominant phases gradually. From the change of equilibria phase relations, it is evident that the increase of Al_2O_3 addition certainly have great influence on equilibria phases, which will lead to the Ti-rich phase change from $\text{CaO} \cdot \text{TiO}_2$ phase to Al–Ti diopside solid solution phase or pseudobrookite solid solution phase.

4. Conclusion

In order to solve the situation of there is not enough thermodynamic data related to the comprehensive utilization of Ti-bearing slag and other Ti-containing resources, the equilibria phase relations of $\text{CaO} \cdot \text{SiO}_2 \cdot 5\text{wt}\% \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ system with up to 30 wt% Al_2O_3 at $w(\text{CaO})/w(\text{SiO}_2)$ of 1.00 were experimental determined by high temperature thermodynamic equilibria technique followed by rapid quenching at 1 300°C and 1 400°C. The equilibria phase assemblies and phase compositions were analyzed by XRD (X-Ray diffraction) and SEM-EDX (Scanning Electron Microscope and Energy Dispersive X-ray Fluorescence scope), and the equilibria phases results indicated that with the increase of Al_2O_3 content the coexisting equilibria solid phases gradually change from melilite solid solution $((2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2, 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)_{\text{ss}})$ and perovskite $(\text{CaO} \cdot \text{TiO}_2)$ to Al–Ti diopside solid solution $(\text{Ca}(\text{Ti}, \text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6)$, spinel $(\text{MgO} \cdot \text{Al}_2\text{O}_3)$, and pseudobrookite solid solution $(\text{MgO} \cdot \text{TiO}_2, \text{Al}_2\text{O}_3 \cdot \text{TiO}_2)_{\text{ss}}$. Meanwhile, comparisons of the predictions by Factsage 7.2 indicated that the calculated equilibria phase relations were only well agree with experimental results below 20 wt% Al_2O_3 and TiO_2 content, while great deviations presented when Al_2O_3 content higher than 20 wt%. Based on the experimental and calculated results, the 1 300°C and 1 400°C liquidus lines as well as the predicted phase boundary lines were constructed for the specific composition range of $\text{CaO} \cdot \text{SiO}_2 \cdot 5\text{wt}\% \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ system.

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