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Phase equilibria of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system in air at 1250-1400 °C

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Abstract

The equilibrium phase relations of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system were investigated experimentally in air at 1250-1400 °C using a high-temperature equilibration/quenching technique, followed by direct phase analysis by scanning electron microscopy equipped with X-ray energy dispersive spectroscopy. The equilibrium solid phases of silica, rutile, and pseudobrookite solid solution were found to coexist with the liquid phase. The 1300-1400 °C isothermal sections were constructed based on the experimentally measured liquid compositions. The experimental results were compared with simulations using MTDATA and FactSage thermodynamic software and their databases. This study provides guidelines for the selective crystallization of pseudobrookite from titania-bearing slag.

Keywords: Phase equilibria; thermodynamic; titania-bearing slag; liquidus temperature; circular economy

1. Introduction

Titania-bearing slag is a typical industrial byproduct of the blast furnace smelting of vanadium and titanium magnetites [1], where the TiO_2 content is approximately 22-25 wt% [2-4] and indicates a good source of titania. With a greater demand for a circular economy, various techniques, such as selective crystallization of TiO_2 -rich crystals followed by phase separation (SCPS), hydrometallurgical acid leaching, and the melting reduction method [5-12], have been developed so far for effective recovery of the titania values from titania-bearing slags. Of these, the SCPS method was suggested to have the most industrial potential for slag processing [13].

The components of titania-bearing slags in air can be described by the CaO-SiO₂-TiO₂-Al₂O₃-MgO system [13, 14]. Rutile, perovskite, and pseudobrookite are the main TiO₂-rich mineral phases in the system. The selective enrichment of TiO₂ into perovskite has been extensively investigated by many researchers [3, 15-24], but limited efforts have been devoted to the crystallization of rutile and pseudobrookite [3, 9, 12, 25]. Compared with the mineral phases of rutile and pseudobrookite, the low theoretical content of TiO₂ in perovskite, approximately 58 wt%, as well as its dendrite structure and similar density to other phases, suggest that perovskite is not an ideal choice for recovering titania from Ti-bearing slags [9]. In contrast, pseudobrookite has the advantages of a high theoretical TiO₂ content (more than 70%) and higher density (4.19 g cm⁻³) than that of the glass phase (2.8 g cm⁻³) [3]. Therefore, it is appropriate to enrich the TiO₂ into the pseudobrookite phase. To obtain further information about the precipitation conditions of pseudobrookite in slag, it is essential to characterize the pseudobrookite primary phase field in the CaO-SiO₂-TiO₂-Al₂O₃-MgO system by constructing a detailed phase diagram.

Goso et al. [14] obtained the phase equilibria and liquidus surface of the 19.69 wt% SiO₂-37.19 wt% TiO₂-13.12 wt% Al₂O₃-30.00 wt% (CaO+MgO) system at P_{O2} of 10⁻¹⁶ to 0.21 atm using FactSage simulation. The spinel solution ((Mg)(Al, Ti)O₄) was found to precipitate as the primary phase with higher MgO content, whereas the crystallization of pseudobrookite solution (MgTi₂O₅-Al₂TiO₅) took place when the P_{O2} ranged between 10⁻¹⁰ and 10⁻¹⁵ atm. Wang et al. [26] investigated the phase equilibria of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system with constant 10 wt% Al₂O₃ and 5 wt% MgO at 1500 °C. The primary phase field of anosovite (i.e., the pseudobrookite solid solution in the present study) in the TiO₂-rich corner was obtained. The phase relations of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system with fixed 5-10 wt% MgO and 10-30 wt% Al₂O₃ at 1250-1500 °C were systematically studied by Shi et al. [27-32] and Sun et al. [33-35]. They paid a lot of attention to the perovskite primary phase field. However, the TiO₂-enriched pseudobrookite solid solution (MgO·2TiO₂, Al₂O₃·TiO₂)_{ss}) was observed in only a limited number of studies [27-30]. Osborn et al. [36] investigated the liquidus temperatures of the CaO-MgO-Al₂O₃-TiO₂-SiO₂ system on different Al₂O₃-TiO₂ levels: 10 wt% Al₂O₃-2.5 wt% TiO₂, 10 wt% Al₂O₃-5 wt% TiO₂, 10 wt% Al₂O₃-10 wt% TiO₂, and 15 wt% Al₂O₃-2.5 wt% TiO₂. Zhao et al. [37] studied the TiO₂-CaO-MgO-Al₂O₃-SiO₂ system with fixed (CaO/MgO) and (Al₂O₃/SiO₂) ratios at carbon saturation. The isotherms in the perovskite and pseudobrookite $(2(Ti^{3+}, Mg^{2+}, Al^{3+}) \cdot Ti^{4+}O_5)$ primary phase fields were constructed in a TiO₂-(CaO+MgO)-(SiO₂+Al₂O₃) pseudo-ternary phase diagram.

Although the phase equilibria of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system have been investigated to some extent, there remain many gaps and inconsistencies in the knowledge base about the phase relations of the system, and detailed composition ranges for the precipitation of pseudobrookite are far from sufficient. Therefore, this study was initiated with the focus on the phase equilibria of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system at 1250-1400 °C

in air. Based on the typical industrial composition of Ti-bearing slags [1, 2, 5], the Al_2O_3 and MgO contents in the initial slag mixtures were designed to be 15 wt% and 10 wt%, respectively. This study will provide useful information for the selective crystallization of the pseudobrookite phase.

2. Experimental

High purity powders of CaO (Sigma-Aldrich, 99.9 wt%), SiO₂ (Alfa Aesar, 99.995 wt%), Al₂O₃ (Sigma-Aldrich, 99.99 wt%), MgO (Alfa Aesar, 99.995 wt%), and TiO₂ (Sigma-Aldrich, 99.8 wt%) were used as starting materials. Each powder was weighed in a certain proportion, mixed thoroughly in an agate mortar, and then pressed into a pellet.

The high-temperature equilibration of the oxide mixtures was carried out in a vertical, impervious alumina tube furnace, as shown in Figure 1, followed by quenching in an ice-water mixture [38]. The furnace temperature was regulated using a Eurotherm 3216 PID controller with an uncertainty of ± 3 °C. The sample pellet was placed in a crucible made of platinum foil and held in the center of the uniform temperature hot zone by a platinum wire from the top of the furnace. An alumina-shielded S-type Pt/Pt-10%Rh thermocouple placed next to the sample was employed for monitoring the sample temperature. The thermocouple was calibrated beforehand at the factory with a maximum deviation from standard of ± 2 °C [39]. For each experiment, approximately 0.15 g of slag was equilibrated at the experimental temperature (1250-1400 °C) for at least 48 hours [27, 29, 40]. After equilibration, the samples were released, dropped under gravity, and were quenched in an ice-water mixture. Detailed information about the experimental furnace and procedures was provided in our previous study [40].



Fig. 1. Schematic cross-section of experimental furnace.

The quenched samples were dried at ambient temperature post quenching, mounted in epoxy resin, ground and polished using a metallographic polishing cloth with a diamond spray. The polished surfaces of the samples were carbon-coated to ensure good electrical conductivity. The equilibrium phase compositions were analyzed using a Tescan MIRA 3 scanning electron microscope (SEM, Tescan, Brno, Czech Republic) equipped with an UltraDry silicon drift energy dispersive X-ray spectrometer (EDS, Thermo Fisher Scientific, Waltham, MA, USA) and NSS microanalysis software. The analytical settings for SEM-EDS are an accelerating voltage of 15 kV, beam current of 20 nA, and working distance of 20 mm. The standards and analyzed X-ray lines in the EDS analysis were as follows: olivine (for O, K α), quartz (for Si, K α), metal Al (for Al, K α), metal Mg (for Mg, K α), calcite (for Ca, K α), and metal Ti (for Ti, K α). At least eight points were measured for each phase to ensure high statistical reliability. The Proza (Phi-Rho-Z) on-line matrix correction program [41] was employed for raw data processing before normalizing the results.

Code	Temperature/°C	Initial composition/wt%					Equilibrium aboasa	Equilibrium composition/wt%				
		TiO ₂	SiO_2	CaO	MgO	Al_2O_3	Equilibrium phases	TiO ₂	SiO ₂	CaO	MgO	Al ₂ O ₃
E1	1250	5.00	58.33	11.67	10.00	15.00	L	$5.3(5) \pm 0.37$	$61.5(8) \pm 1.63$	$10.7(4) \pm 0.11$	$7.8(0) \pm 0.76$	$14.5(3) \pm 0.45$
							Silica	$0.0(5) \pm 0.05$	$99.9(5) \pm 0.05$	-	-	-
E3	1250	5.00	43.75	26.25	10.00	15.00	L	$5.3(0) \pm 0.12$	$47.7(3) \pm 0.30$	$25.9(2) \pm 0.13$	$7.4(5) \pm 0.15$	$13.6(0) \pm 0.18$
E4	1250	15.00	50.00	10.00	10.00	15.00	L	$10.0(2) \pm 0.71$	$59.8(0) \pm 2.52$	$9.8(1) \pm 0.46$	$7.2(5) \pm 0.58$	$13.1(2) \pm 0.79$
							Silica	$0.0(2) \pm 0.03$	$99.9(7) \pm 0.03$	-	-	-
							Rutile	$99.0(5) \pm 0.18$	$0.2(3) \pm 0.04$	$0.2(5) \pm 0.11$	$0.0(3) \pm 0.02$	$0.4(4) \pm 0.05$
							Pseudobrookite	$76.7(0) \pm 0.25$	$0.4(2) \pm 0.03$	$0.1(9) \pm 0.06$	$17.2(0) \pm 0.12$	$5.5(0) \pm 0.32$
E5	1250	15.00	42.86	17.14	10.00	15.00	L	$15.3(8) \pm 0.10$	$46.2(4) \pm 0.06$	$16.8(7) \pm 0.03$	$7.6(4) \pm 0.07$	$13.8(7) \pm 0.06$
E6	1250	15.00	37.50	22.50	10.00	15.00	L	$15.6(2) \pm 0.12$	$41.5(3) \pm 0.09$	$21.9(8) \pm 0.07$	$7.1(5) \pm 0.04$	$13.7(1) \pm 0.13$
E7	1250	25.00	41.67	8.33	10.00	15.00	L	$10.7(2) \pm 0.37$	$54.9(5) \pm 0.31$	$10.7(9) \pm 0.30$	$7.2(8) \pm 0.46$	$16.2(6) \pm 0.10$
							Rutile	$98.8(4) \pm 0.16$	$0.2(7) \pm 0.06$	$0.3(6) \pm 0.10$	$0.0(3) \pm 0.02$	$0.5(0) \pm 0.04$
							Pseudobrookite	$74.9(6) \pm 0.82$	$0.7(6) \pm 0.73$	$0.3(2) \pm 0.20$	$16.2(7) \pm 0.43$	$7.6(8) \pm 0.50$
E13	1250	45.00	25.00	5.00	10.00	15.00	L	$10.4(1) \pm 0.05$	$54.4(6) \pm 0.27$	$11.1(5) \pm 0.04$	$4.9(8) \pm 0.17$	$19.0(0) \pm 0.42$
							Rutile	$98.9(2) \pm 0.10$	$0.2(1) \pm 0.04$	$0.2(0) \pm 0.10$	$0.0(4) \pm 0.02$	$0.6(4) \pm 0.04$
							Pseudobrookite	$73.0(6) \pm 0.82$	$0.4(6) \pm 0.06$	$0.2(7) \pm 0.10$	$14.7(2) \pm 0.44$	$11.4(9) \pm 1.19$
E7	1300	25.00	41.67	8.33	10.00	15.00	L	$14.2(3) \pm 0.51$	$52.7(7) \pm 0.89$	$10.8(1) \pm 0.34$	$6.4(5) \pm 0.11$	$15.7(3) \pm 0.95$
							Rutile	$98.9(3) \pm 0.18$	$0.2(5) \pm 0.05$	$0.2(9) \pm 0.14$	$0.0(3) \pm 0.02$	$0.5(0) \pm 0.04$
							Pseudobrookite	$76.1(6) \pm 0.99$	$0.4(7) \pm 0.04$	$0.2(0) \pm 0.06$	$16.6(8) \pm 0.45$	$6.4(9) \pm 1.39$
E8	1300	25.00	35.71	14.29	10.00	15.00	L	$23.3(4) \pm 0.12$	$39.7(7) \pm 0.16$	$16.0(9) \pm 0.04$	$7.1(5) \pm 0.11$	$13.6(5) \pm 0.06$
E9	1300	25.00	31.25	18.75	10.00	15.00	L	$25.4(2) \pm 0.07$	$34.2(9) \pm 0.20$	$19.2(5) \pm 0.04$	$7.4(0) \pm 0.10$	$13.6(5) \pm 0.05$
E10	1300	35.00	33.33	6.67	10.00	15.00	L	$14.1(2) \pm 0.15$	$52.1(8) \pm 0.58$	$9.8(7) \pm 0.08$	$7.5(1) \pm 0.33$	$16.3(2) \pm 0.31$
							Rutile	$98.9(8) \pm 0.11$	$0.2(1) \pm 0.03$	$0.1(6) \pm 0.07$	$0.0(4) \pm 0.02$	$0.6(1) \pm 0.04$
							Pseudobrookite	$74.7(0) \pm 0.19$	$0.4(7) \pm 0.04$	$0.2(1) \pm 0.05$	$15.7(8) \pm 0.10$	$8.8(3) \pm 0.21$
E11	1300	35.00	28.57	11.43	10.00	15.00	L	$22.4(9) \pm 0.18$	$40.9(7) \pm 0.16$	$15.2(7) \pm 0.06$	$5.8(9) \pm 0.15$	$15.3(9) \pm 0.19$
							Rutile	$98.7(8) \pm 0.16$	$0.2(5) \pm 0.09$	$0.2(8) \pm 0.11$	$0.0(5) \pm 0.03$	$0.6(5) \pm 0.05$
							Pseudobrookite	$74.1(3) \pm 0.34$	$0.4(0) \pm 0.03$	$0.2(4) \pm 0.09$	$16.8(0) \pm 0.22$	$8.4(2) \pm 0.57$
E12	1300	35.00	25.00	15.00	10.00	15.00	L	$28.1(0) \pm 0.18$	$32.5(8) \pm 0.13$	$17.8(9) \pm 0.08$	$6.2(5) \pm 0.12$	$15.1(9) \pm 0.10$
							Rutile	$98.9(9) \pm 0.05$	$0.2(1) \pm 0.02$	$0.1(9) \pm 0.04$	$0.0(3) \pm 0.01$	$0.5(8) \pm 0.02$
							Pseudobrookite	$72.8(8) \pm 0.50$	$0.4(0) \pm 0.03$	$0.2(8) \pm 0.08$	$16.2(3) \pm 0.25$	$10.2(2) \pm 0.71$
E13	1300	45.00	25.00	5.00	10.00	15.00	L	$13.0(6) \pm 0.11$	$51.4(9) \pm 0.25$	$10.1(9) \pm 0.12$	$5.8(1) \pm 0.04$	$19.4(4) \pm 0.03$
							Rutile	$98.7(5) \pm 0.11$	$0.2(2) \pm 0.05$	$0.2(2) \pm 0.06$	$0.0(3) \pm 0.02$	$0.7(7) \pm 0.03$
							Pseudobrookite	$70.2(2) \pm 1.09$	$0.4(4) \pm 0.02$	$0.1(5) \pm 0.03$	$14.3(5) \pm 0.63$	$14.8(3) \pm 1.70$
E13	1400	45.00	25.00	5.00	10.00	15.00	L	$32.6(9) \pm 0.23$	$37.4(8) \pm 0.19$	$9.1(9) \pm 0.17$	$4.4(4) \pm 0.08$	$16.2(0) \pm 0.13$
							Pseudobrookite	$74.3(0) \pm 0.44$	$0.3(7) \pm 0.04$	$0.0(7) \pm 0.02$	$16.2(8) \pm 0.23$	$8.9(8) \pm 0.65$
E14	1400	45.00	21.43	8.57	10.00	15.00	L	$41.0(9) \pm 0.18$	$25.5(8) \pm 0.13$	$11.9(0) \pm 0.08$	$6.8(8) \pm 0.04$	$14.5(4) \pm 0.09$
E15	1400	45.00	18.75	11.25	10.00	15.00	L	$43.1(7) \pm 0.08$	$21.3(7) \pm 0.06$	$13.7(3) \pm 0.04$	$7.4(0) \pm 0.08$	$14.3(3) \pm 0.05$
E16	1400	55.00	16.67	3.33	10.00	15.00	L	$44.3(2) \pm 0.18$	$28.4(5) \pm 0.22$	$8.0(4) \pm 0.20$	$3.3(9) \pm 0.20$	$15.8(0) \pm 0.10$
							Rutile	$98.9(5) \pm 0.08$	$0.1(6) \pm 0.02$	$0.0(5) \pm 0.02$	$0.0(5) \pm 0.02$	$0.8(0) \pm 0.05$
							Pseudobrookite	$72.4(9) \pm 0.45$	$0.3(5) \pm 0.03$	$0.0(7) \pm 0.01$	$15.2(6) \pm 0.32$	$11.8(4) \pm 0.76$
E17	1400	55.00	14.29	5.71	10.00	15.00	L	$46.9(5) \pm 1.28$	$22.4(7) \pm 1.01$	$11.1(1) \pm 0.16$	$4.6(7) \pm 0.19$	$14.7(9) \pm 0.45$
-	1.400		10		10.00		Pseudobrookite	$73.0(1) \pm 0.46$	$0.3(8) \pm 0.04$	$0.1(4) \pm 0.05$	$15.0(9) \pm 0.25$	$11.3(8) \pm 0.68$
E18	1400	55.00	12.50	7.50	10.00	15.00	L	$47.5(2) \pm 0.57$	$19.5(8) \pm 0.48$	$12.6(8) \pm 0.46$	$5.1(7) \pm 0.30$	$15.0(6) \pm 0.23$
							Pseudobrookite	$71.6(7) \pm 0.57$	$0.4(1) \pm 0.09$	$0.1(6) \pm 0.06$	$15.0(8) \pm 0.33$	$12.6(8) \pm 0.83$

Table 1. Experimentally determined equilibrium phase compositions for the CaO-SiO₂-TiO₂-Al₂O₃-MgO system equilibrated with air ($P_{O2} = 10^{-0.6778}$ atm) at 1250-1400 °C.

3. Results and Discussion

The equilibrium phase compositions and typical microstructures of the samples obtained at 1250-1400 °C are shown in Table 1 and Figures 2-4, respectively. As the accuracy of EDS analysis is one decimal digit unit only, therefore, the second decimal digit was listed in the bracket. It should be noted that the designed slag compositions were not used for constructing the phase diagram so that the water contamination before the equilibration can be eliminated. Based on the prediction of the titanium oxide predominance phase diagram [40], titanium presented a valence state of Ti^{4+} in air, in the conditions of the present study. Therefore, the concentrations of titanium oxide were calculated from the EDS analyses and presented as TiO_2 .

3.1 Phase relations at 1250-1400 °C

The equilibrium results at 1250 °C were more complicated compared with those at 1300 and 1400 °C. Single liquid phase domains and multiphase equilibria of two, three, and four phases were observed. Figures 2(a)-2(c) show typical microstructures of liquid-silica, homogeneous liquid, and liquid-rutile-pseudobrookite equilibria, respectively. A four-phase equilibrium, i.e., liquid-silica-rutile-pseudobrookite, was confirmed in sample E4 (Figure 2(d)). As the sample broke into tiny pieces in quenching, the three-phase equilibria of liquid-rutile-pseudobrookite and two-phase equilibria of liquid-silica were found in different parts of the sample, as shown in Figures 2(d1) and 2(d2), respectively, indicating that the primary phase fields of silica, rutile, and pseudobrookite are adjacent to each other.



Fig. 2. Typical SEM back-scattered electron images showing the microstructures of equilibrium phases obtained at 1250 °C; L-liquid phase.

Figure 3 shows the representative microstructures obtained at 1300 °C. Due to the limited experimental points, only the single liquid oxide phase and the three-phase equilibrium of liquid-rutile-pseudobrookite were observed. Sample E9 in Figure 3(a) displays a single phase with no observation of primary crystals. The white phase in Figure 3(b) was identified as rutile, and the light gray and dark gray matrix phases were designated as the pseudobrookite and quenched, glassy liquid oxide phase, respectively.



Fig. 3. Typical SEM back-scattered electron images showing the microstructures of equilibrium phases obtained at 1300 °C; L-liquid phase.

As for sample E13, it is interesting to observe that the liquid-rutile-pseudobrookite three-phase equilibria at 1300 °C was transformed into a two-phase equilibrium of liquid-pseudobrookite when the temperature was increased to 1400 °C. It can be seen in Figure 4(a) that the size of the pseudobrookite crystals precipitated in the primary phase field of pseudobrookite was relatively large (> 50μ m), indicating that it is favorable for the application of the selective crystallization and phase separation (SCPS) method [12, 34]. An example of a single liquid oxide phase was found in sample E14 and is illustrated in Figure 4(b). A three-phase equilibrium was confirmed in sample E16 with the liquid oxide matrix coexisting with the rutile and pseudobrookite phases.



Fig. 4. Typical SEM back-scattered electron images showing the microstructures of equilibrium phases obtained at 1400 °C; L-liquid phase.

3.2 Comparison between experimental and computational results

As can be observed in Table 1, the MgO and Al_2O_3 contents in the liquid phase were approximately 8 wt% and 14 wt%, respectively. Due to the precipitation of MgO-containing crystals (i.e., the pseudobrookite solid solution) from the liquid phase of the system, the MgO and Al_2O_3 contents in the liquid phase of the quenched samples could not lie exactly on the designed contents of 10 wt% MgO and 15 wt% Al_2O_3 , respectively. Therefore, the experimentally measured liquid compositions obtained at 1250-1400 °C in the present study were plotted onto the quasiternary CaO-SiO₂-TiO₂-14 wt% Al_2O_3 -8 wt% MgO system, as shown in Figures 5-7. Based on the measured liquid compositions, the 1300 and 1400 °C isothermal sections were constructed.

The liquid composition was normalized before being depicted on the quasiternary phase diagram using the following steps: (1) the MgO and Al_2O_3 contents were recalculated to 8 wt% and 14 wt%, respectively; and (2) the total of CaO, SiO₂, and TiO₂ was normalized to 78 wt% with their original individual proportions. The experimental data from the literature [27, 29, 44, 45], the simulation results from FactSage [46] using the "FactPS" and "FToxid" databases, and from MTDATA [42, 43] with the MTOX database [43] were also projected onto the phase diagram for comparison.

Figure 5 shows the comparison of the present experimental results obtained at 1250 °C with the simulations by FactSage (Figure 5(a)) and MTDATA (Figure 5(b)). It was found that the liquidus domain measured experimentally by Shi et al. [27] agreed more consistently with the prediction by MTDATA, whereas the liquid phase domain simulated by FactSage was significantly larger, expanding toward the area with either a higher TiO_2 or SiO_2 content. The present results in the silica primary phase field were slightly on the higher side of the predictions by FactSage, shifting toward the SiO_2 corner. The 1250 °C liquidus domain obtained in the present study is significantly larger than the calculations by MTDATA, which show slightly too high liquidus contour temperatures for the feldspar primary phase field ($Al_2CaSi_2O_8$, the same phase as anorthite in FactSage) by only 15-25 °C compared with the present data.

Figure 6 shows the constructed 1300 °C isotherm based on the present experimentally measured liquid compositions. The results by Shi et al. [29] agree well with the data in the literature [44, 45]. The results in the perovskite primary phase field [29] fit well with the predictions by both FactSage and MTDATA. The 1300 °C isotherm constructed in the pseudobrookite primary phase field in the present study agrees well with the observations by Shi et al. [29], shifting slightly toward a higher TiO₂ content region when compared with the simulation by MTDATA. However, the pseudobrookite primary phase field was not observed in the calculations by FactSage, and the 1300 °C isotherm constructed according to the present results as well as the results by Shi et al. [29] shows a smaller liquid phase domain compared with the FactSage predictions.

The 1400 °C isotherm in Figure 7 obtained by Shi et al. [29] fits well with the predictions by FactSage and MTDATA in the perovskite primary phase field. However, the results obtained in the pseudobrookite primary phase field in the present study have significant discrepancies with the simulations. The present 1400 °C isotherm in the pseudobrookite primary phase field has a lower CaO content, compared with the prediction by MTDATA. To adjust the Ti-bearing slag composition based on the guideline of the phase diagram, further efforts are needed for accurate determination of the pseudobrookite primary phase field in the CaO-SiO₂-TiO₂-Al₂O₃-MgO system.





Fig. 5. A comparison of the equilibrium liquid domain compositions obtained at 1250 °C with the simulations by FactSage (a) and MTDATA (b) superimposed; CaO·Al₂O₃·2SiO₂-feldspar, the same phase as anorthite in FactSage.





Fig. 6. A comparison of the equilibrium liquid domain compositions obtained at 1300 °C with the simulations by FactSage (a) and MTDATA (b) superimposed.





Fig. 7. A comparison of the equilibrium liquid domain compositions obtained at 1400 °C with the simulations by FactSage (a) and MTDATA (b) superimposed.

4. Conclusions and Summary

The phase relations of the CaO-SiO₂-TiO₂-Al₂O₃-MgO system at 1250-1400 °C were experimentally investigated in equilibrium with air using the high-temperature equilibration/quenching/SEM-EDS in situ phase analysis method. The silica primary phase, rutile primary phase, and pseudobrookite solid solution primary phase were observed. Based on the current experimental results as well as the data from the literature, 1300 and 1400 °C CaO-SiO₂-TiO₂-14 wt% Al₂O₃-8 wt% MgO quasiternary phase diagram isotherms were constructed, which will serve as guidelines for the slag composition optimization by adding slag modifiers or adjusting temperature for selective crystallization of pseudobrookite solid solution and recovery of titania from slag. The present results provide fundamental information for further systematic study on the phase relations of titania-bearing slag systems.

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Declaration of interests

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□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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