High Temperature Phase Relations in FeO_X ($X = 1$ and 1.33)– CaO – SiO_2 Systems under Various Oxygen Partial Pressure

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As a fundamental study of slags in metallurgical processes, liquidus lines in the FeO (wüstite)– CaO – SiO_2 and Fe_3O_4 (spinel)– CaO – SiO_2 systems were determined at temperatures between 1573 and 1673 K and partial pressures of oxygen between 10^{-4} and 36 Pa using a quenching method with a crucible of platinum foil. It was found that the two phases (solid wüstite and liquid) region in the FeO – CaO – SiO_2 system (1573 K) increased remarkably by changing the partial pressure of oxygen from 10^{-4} to 10^{-3} Pa. It was also found that the two phases (solid spinel and liquid) region in the Fe_3O_4 – CaO – SiO_2 system (1573 K) at $p\text{O}_2$ of 10^{-2} Pa was a little larger than that in the FeO – CaO – SiO_2 system at $p\text{O}_2$ of 10^{-3} Pa but it was extended considerably when the oxygen pressure was increased to 10^{-1} Pa. However, the two liquids region did not change too much in the range of oxygen pressure above 10^{-1} Pa even though the liquidus line became almost parallel to the Fe_3O_4 – CaO axis in the ternary diagram when the oxygen pressure was increased. Furthermore, it was found that the two phase region in the Fe_3O_4 – CaO – SiO_2 system at $p\text{O}_2$ of 10^{-1} Pa decreased remarkably with increasing temperature. On the basis of the obtained and reported data, the homogeneous liquid regions in the FeO_X – CaO – SiO_2 systems (1573 K) at $p\text{O}_2$ of 10^{-3} Pa, 10^{-1} Pa and in air were compared.

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1. Introduction

The FeO_X – CaO – SiO_2 base slag is used in the treatment of wastes and in the slag cleaning since it removes arsenic and antimony more effectively than the iron silicate slags and removes lead better than the ferrite slags. The FeO_X – CaO – SiO_2 base slag is also considered an option for use in a new type of copper smelting such as in direct blister copper making¹⁾ since this slag, besides its ability to remove impurities, presents a minimum loss of copper as oxidic dissolution.²⁾ Copper smelting is carried out at oxygen partial pressures from 10^{-8} to 10^{-6} (the partial pressure expressed as dimensionless one, defined by $p\text{O}_2 = P\text{O}_2 \text{ Pa} / 101325 \text{ Pa}$).

Despite of the industrial importance of this slag system at intermediate oxygen partial pressures, little is known about the system except at the extremely reductive conditions at iron saturation and the oxidative condition in air.^{3,4)} Shigaki *et al.*⁵⁾ reported the liquid surface at 1573 K and $p\text{O}_2$ of 10^{-7} . Kimura *et al.*⁶⁾ reported the liquid isotherms at 1573 K around $p\text{O}_2$ of 10^{-8} , 10^{-7} and 10^{-6} . In addition to these experimental works, the liquidus surface of FeO_X – CaO – SiO_2 base slags at intermediate oxygen partial pressures in industrial processes has been recently quantified by different authors.^{7–9)} The results of Kimura *et al.*⁶⁾ show some incongruence in the FeO_X corner, where an increase in the oxygen partial pressure decreases the stable region of wüstite. The results of one physicochemical modelling^{7,8)} agree partially with the experimental data of Kimura *et al.*⁶⁾ and partially disagree with the results of Muan *et al.*¹⁰⁾ in the FeO – Fe_2O_3 – SiO_2 system. In addition, there are some disagreements between the reported results of computer thermodynamical or physicochemical modelling obtained by different authors.^{7–9)}

The objective of the present work is to determine the liquidus in the FeO (wüstite)– CaO – SiO_2 and Fe_3O_4 (spinel)– CaO – SiO_2 slags at the intermediate $p\text{O}_2$ of 3.63×10^{-4} to 10^{-9} at 1573–1673 K, putting emphasis on the behaviour in

the FeO or Fe_3O_4 corner. The obtained information will provide additional data to clarify various disagreements in the literature. Also, the obtained phase diagrams will be useful in the metallurgical industry to assist in the selection of slag chemistry, the operation conditions and the development of new processes.

2. Experimental Method and Procedure

The experiments were conducted for (1) the FeO (wüstite)– CaO – SiO_2 system at 1573 K and $p\text{O}_2$ of 10^{-9} and 10^{-8} , (2) the Fe_3O_4 (spinel)– CaO – SiO_2 system at 1573 K and $p\text{O}_2$ of 10^{-7} , 10^{-6} , 10^{-5} and 3.63×10^{-4} , and (3) the Fe_3O_4 – CaO – SiO_2 system at 1573, 1623 and 1673 K at $p\text{O}_2$ of 10^{-6} . The Fe_2O_3 – CaO – SiO_2 system at 1573 K in air was also investigated in a preliminary experiment to validate the present experimental method and procedure.

The temperature of a sample was controlled within 2 K by a SCR controller with a Pt/Pt–Rh thermocouple. CO_2 – CO gas mixtures were used to control the partial pressure of oxygen according to the reaction

Pure CO_2 was used for the experiments at $p\text{O}_2$ of 3.63×10^{-4} , while the N_2 – O_2 gas mixture was used for the air condition. The flow rate of gas mixture, which was regulated using a capillary flow-meter, was introduced into the reaction chamber through an alumina tube with a flow rate of $1.7 \times 10^{-6} \text{ m}^3/\text{s}$. The phase relations were determined by the quenching method. A pre-melted FeO_X – CaO – SiO_2 mother slag was mixed with Fe_2O_3 , CaO and SiO_2 to obtain the required initial composition and was held in a platinum foil crucible with 20 mm height, 6 mm diameter and 0.03 mm thickness. The sample was heated at the desired temperature and oxygen pressure for a period of 86.4 ks when the

Fig. 1 Analysis of glassy slag composition (A: wüstite, B: glassy slag).

equilibration was made. Then, it was taken out of the furnace and quenched in a jet stream of argon. One vertical section of the quenched sample was mounted on epoxy resin and polished for Electron Probe Micro Analysis (EPMA). Optical microscopy was employed to identify the phases present in the sample. The crystal composition was confirmed by XRD-Diffraction. Some selected samples were also analyzed by Inductively Coupled Plasma Spectrometry (ICP). The analysis of the glassy slag by EPMA was carried out at more than 8 different places on each sample, each covering an area of $100\mu\text{m} \times 100\mu\text{m}$ as indicated in Fig. 1(a).

Special attention was paid to ensure the accuracy of the present experimental method and procedure, and they were corroborated in a number of different ways. Firstly, the samples quenched from the homogeneous liquid phase were analyzed by EPMA and ICP. It was found that both results showed a good agreement within a range of 2 mass%. Secondly, a set of experiments to approach to the liquid phase from the FeO corner along a given CaO/SiO_2 ratio showed that the liquidus point was the same between these experimental runs. As shown in Fig. 1(c), the initial bulk compositions are represented by the solid points 1 and 2, and the corresponding glassy slag compositions at equilibrium are represented by the open circles. The density and size of the crystals, which are shown in the microphotograph, increased despite there being no appreciable variation in the composition of the glassy slag (liquidus composition). Thirdly, the experiments in air were carried out at 1573 K for the liquidus of Fe_2O_3 – CaO – SiO_2 slag in the Fe_2O_3 corner. As indicated in Fig. 2, the present experimental results agree well with those obtained by Phillips *et al.*¹²⁾ and Pownceby *et al.*⁴⁾

The present experimental technique has been already

Fig. 2 Liquidus in the Fe_2O_3 corner of Fe_2O_3 – CaO – SiO_2 slag at 1573 K in air (stable iron oxide: Fe_2O_3).

proven to be successful in providing accurate phase equilibrium data.^{4,13)} Some important advantages of this technique are that the changes in the bulk composition during equilibration do not affect the final results, and that each experiment provides useful information on both the liquidus composition and the compositions of the solid phases formed. This gives a remarkable improvement in the experimental efficiency.

Some preliminary experiments were carried out to determine the time required for the equilibration between the slag and the platinum crucible. Figure 3 shows the EPMA profile for a cross-section in the platinum foil of crucible. At the holding time of 86.4 ks, the profile of iron is almost constant against the cross-section. Thus, it was clarified that the equilibrium with the platinum crucible could be made in a restricted time of less than 86.4 ks. The equilibrium inside the

Fig. 3 Profiles of platinum and iron concentrations in a cross section of platinum foil at 1573 K and pO_2 of 10^{-8} at different holding times (The left and right sides present the out side and inside of the platinum crucible, respectively).

slag was also confirmed by the uniformity in the compositions of both the glassy slag and the solid phases.

There was usually no difficulty in distinguishing primary crystals, which were grown in equilibrium with the melt, from the corresponding crystals formed during quenching. However, for the compositions close to the binary Fe_3O_4 –CaO or FeO –CaO join, in some cases, the quenched crystals of $2CaO \cdot Fe_2O_3$ were difficult to distinguish from the primary ones. Furthermore, in the range of higher silica content where $CaO \cdot SiO_2$ is supposed to appear, irregular-shaped SiO_2 particles were observed. This may indicate that the conditions are not in equilibrium. Therefore, the liquidus line in equilibrium with $CaO \cdot SiO_2$ was evaluated from the results for the homogeneous liquid where the addition of another 2 mass% SiO_2 drastically changed the glassy slag compositions.

3. Results and Discussion

The results of compositional analysis are listed in Tables 1 to 9, along with those for the Fe_2O_3 –CaO– SiO_2 system, corresponding to the systems and the experimental conditions. It was confirmed by XRD for the solidified crystals that wüstite (FeO) is stable at pO_2 of 10^{-9} and 10^{-8} , while spinel (Fe_3O_4) at pO_2 of 10^{-7} , 10^{-6} , 10^{-5} and 3.63×10^{-4} . Hematite (Fe_2O_3) is stable at 1573 K in air.

In these Tables, mass% Fe_2O_3 , Fe_3O_4 and FeO are given by the difference between 100 mass% and the summation of mass% CaO and mass% SiO_2 , which were determined by EPMA. This approach may be justified because it was difficult for EPMA to distinguish the oxidation state of iron in the samples and because the analysis of iron in the same sample scattered more than that of CaO or SiO_2 .

It is indicated in the compositional analysis of solid phases that spinel ($(Fe, Ca)O \cdot Fe_2O_3$) contains small amounts of SiO_2 less than 0.5 mass% and CaO less than 0.2 mass%, while wüstite ($(Fe, Ca)O$) less than 0.6 mass% SiO_2 and 1 mass% of CaO. It is also indicated that the crystals of dicalcium ferrite ($2CaO \cdot Fe_2O_3$) and dicalcium silicate ($2CaO \cdot SiO_2$)

Table 1 Composition (mass%) of Fe_2O_3 –CaO– SiO_2 slag at 1573 K in air.

No.	Fe_2O_3	CaO	SiO_2	Phases
1-1	39.1	24.5	36.4	liquid+hematite
1-2	46.4	29.1	24.5	
1-3	42.0	29.2	28.8	
1-4	38.6	19.7	41.7	
1-5	39.9	18.6	41.5	liquid+hematite+tridimite

contain less than 2 mass% SiO_2 and 1 mass% Fe_2O_3 , respectively. Neither iron nor calcium is contained in tridimite (SiO_2).

3.1 FeO –CaO– SiO_2 system

The phase diagram of FeO –CaO– SiO_2 system at 1573 K and pO_2 of 10^{-8} is illustrated in Fig. 4, where two separated liquid regions with the higher and lower contents of SiO_2 are found. It is noted in the higher content region that the liquidus line in the FeO corner (liquid slag equilibrated with the “stable phase FeO ”) remarkably protrudes and is orientated toward the composition of wollastonite ($CaO \cdot SiO_2$). The homogeneous liquid region in the CaO-free FeO – SiO_2 system is between 20 and 40 mass% SiO_2 and, in the FeO –CaO– SiO_2 system, it extends up to the lower content of FeO with about 30 mass% where solid $CaO \cdot SiO_2$ appears. It is noteworthy in the magnified portion of Fig. 4 that the solubility of SiO_2 in another liquid region is considerably small at less than 4 mass%. The liquid region in the SiO_2 -free CaO– FeO system is between 70 and 90 mass% FeO .

Some data are reported for the system at 1573 K and pO_2 of 10^{-8} . The liquidus composition on the SiO_2 side in the FeO – SiO_2 system reported by Muan *et al.*¹⁰⁾ agrees well with the present result, while that on the FeO side reported by the same authors¹⁰⁾ is rather smaller (3~5 mass%) than the present results. The liquidus points on the FeO and $2CaO \cdot Fe_2O_3$ sides obtained by Takeda *et al.*¹⁴⁾ agree fairly well with the present results. The liquidus line reported by Acuña *et al.*¹⁵⁾ at 1573 K and interpolated at pO_2 of 10^{-8} is in

Table 2 Composition (mass%) of FeO–CaO–SiO₂ slag at 1573 K and p_{O_2} of 10^{-8} .

No.	FeO	CaO	SiO ₂	Phases
2-1	78.8	20.6	0.64	liquid
2-2	83.4	15.7	0.84	
2-3	73.4	24.6	2.02	
2-4	62.5	23.1	14.4	
2-5	62.3	21.6	16.2	
2-6	78.4	0	21.7	
2-7	73.7	2.93	23.4	
2-8	63.2	11.0	25.8	
2-9	69.6	0	30.4	
2-10	39.4	29.8	30.9	
2-11	65.3	3.55	31.1	
2-12	54.2	13.9	32.0	
2-13	37.3	30.3	32.4	
2-14	36.2	30.8	33.0	
2-15	45.2	21.3	33.4	
2-16	54.5	8.19	37.3	
3-17	29.4	32.8	37.8	
2-18	34.9	25.5	39.6	
2-19	39.3	20.4	40.3	
2-20	34.6	24.2	41.2	
2-21	39.9	17.8	42.3	
2-22	31.5	25.4	43.1	
2-23	40.1	15.2	44.7	
2-24	32.5	21.0	46.5	
2-25	60.2	0.40	39.4	liquid+tridimite
2-26	53.9	5.49	40.7	
2-27	88.7	11.2	0.06	liquid+wütitite
2-28	87.7	12.0	0.31	
2-29	90.6	8.96	0.44	
2-30	85.5	11.0	1.44	
2-31	85.9	10.9	3.22	
2-32	71.5	17.2	11.3	
2-33	67.8	18.3	13.9	
2-34	80.8	0	19.2	
2-35	80.8	0	19.2	
2-36	67.4	9.60	23.0	
2-37	47.9	27.9	24.2	
2-38	55.5	19.3	25.2	
2-39	57.6	17.0	25.3	
2-40	63.6	10.9	25.4	
2-41	48.9	25.4	25.6	
2-42	54.2	19.9	25.8	
2-43	55.5	18.5	26.0	
2-44	48.0	25.4	26.7	
2-45	54.6	18.5	26.9	
2-46	51.2	19.9	29.0	
2-47	70.2	29.8	0.01	liquid+dicalcium silicate
2-46	70.3	29.7	0.06	
2-47	71.1	28.1	0.83	
2-48	70.1	28.8	1.15	liquid+dicalcium ferrite
2-49	82.2	14.9	2.89	

accordance with the present one in equilibrium with 2CaO·SiO₂.

The numerous data are reported on the phase diagram of

Table 3 Composition (mass%) of FeO–CaO–SiO₂ slag at 1573 K and p_{O_2} of 10^{-9} .

No.	FeO	CaO	SiO ₂	Phases
3-1	83.3	16.2	0.58	liquid
3-2	82.3	14.6	3.09	
3-3	64.0	20.4	15.6	
3-4	88.4	11.5	0.11	liquid+wütitite
3-5	85.0	0	15.0	
3-6	82.0	1.80	16.2	
3-7	77.4	4.48	18.2	
3-8	67.6	12.7	19.7	
3-9	70.7	8.62	20.6	
3-10	57.4	20.8	21.8	

FeO–CaO–SiO₂ system saturated with iron. In Fig. 5, the liquidus regions obtained in the present study are compared with those in the system saturated with iron.¹⁶⁾ It is noteworthy in Fig. 5 that the stable region of solid FeO becomes wider with increasing partial pressure of oxygen from that corresponding to the iron-saturation to 10^{-8} , while the partial pressure has a considerably small effect on the stable region of wollastonite(CaO·SiO₂) and tridimite(SiO₂).

The liquidus line in the FeO corner of FeO–CaO–SiO₂ system was determined at 1573 K and p_{O_2} of 10^{-9} and is shown in Fig. 6(a). As illustrated in Fig. 6(b), the liquidus line at this partial pressure is between those at p_{O_2} of 10^{-8} and the condition of iron-saturation.

3.2 Fe₃O₄–CaO–SiO₂ system

The phase diagram of Fe₃O₄–CaO–SiO₂ system at 1573 K and p_{O_2} of 10^{-6} is illustrated in Fig. 7 where two separated liquid regions with the higher and lower contents of SiO₂ are found. The homogeneous liquid region does not extend in the CaO-free FeO–SiO₂ system and, in the upper region, the content of SiO₂ in the spinel corner remains almost constant at around 35 mass%. It is noteworthy in the magnified portion of Fig. 7 that the solubility of SiO₂ in another liquid region is considerably small at less than 4 mass%. The liquid region in the SiO₂ free CaO–FeO system is between 74 and 82 mass% FeO.

The liquidus line in the Fe₃O₄ corner (liquid slag equilibrated with the “stable phase Fe₃O₄”) of Fe₃O₄–CaO–SiO₂ system was determined at 1573 K and p_{O_2} of 10^{-7} , 10^{-5} and 3.63×10^{-4} . As shown in Fig. 8(a), at p_{O_2} of 10^{-7} , the homogeneous liquid region appears in the CaO-free FeO–SiO₂ system between 22 and 33 mass% of SiO₂. It is shown in Fig. 8(d) that the oxygen pressure have an effect on the stable region of spinel. The effect of p_{O_2} is considerably large between the partial pressures of 10^{-7} and 10^{-6} , and it is mild for the oxygen partial pressures between 10^{-6} and 3.63×10^{-4} . The results for the partial pressures at 10^{-6} and 10^{-5} show an apparent incongruence between them. However, considering the margin of experimental error in the present experimental work, it may be difficult to conclude that there is actually a difference between the results obtained at 10^{-6} and 10^{-5} . It is noteworthy that the liquidus line at p_{O_2} of 10^{-8} and 1573 K, as shown with a dot-line in Fig. 8(d), is fairly close to that at p_{O_2} of 10^{-7} .

Table 4 Composition (mass%) of Fe_3O_4 –CaO– SiO_2 slag at 1573 K and $p\text{O}_2$ of 10^{-6} .

No.	Fe_3O_4	CaO	SiO_2	Phases
4-1	76.2	23.8	0	liquid
4-2	50.7	13.9	37.4	
4-3	38.6	23.0	38.4	
4-4	41.1	20.3	38.7	
4-5	48.9	10.7	40.4	
4-6	34.1	24.3	41.6	
4-7	35.0	18.3	46.7	
4-8	56.8	4.72	38.5	liquid+tridimite
4-9	55.2	5.33	39.5	
5-10	46.7	11.4	42.0	
4-11	44.2	12.1	43.8	liquid+spinel
4-14	81.7	18.3	0	
4-15	81.7	18.4	0	
4-16	81.6	18.4	0.01	
4-17	81.2	18.5	0.28	
4-18	79.2	18.9	1.94	
4-19	33.6	32.2	34.2	
4-20	33.6	32.2	34.2	
4-21	32.3	32.7	35.1	
4-22	32.1	32.8	35.1	
4-23	31.5	33.1	35.4	
4-24	60.5	4.04	35.5	
4-25	59.8	4.76	35.5	
4-26	59.5	4.86	35.7	
4-27	55.5	8.82	35.7	
4-28	55.3	9.05	35.7	
4-29	55.6	8.60	35.8	
4-30	52.8	10.7	36.5	
4-31	46.0	16.6	37.4	
4-32	47.3	15.2	37.5	
4-33	39.9	22.5	37.6	
4-34	37.5	24.5	38.1	
4-35	35.3	26.3	38.4	
4-12	59.0	5.12	35.9	liquid+spinel+tridimite
4-13	57.6	5.97	36.4	liquid+dicalcium ferrite
4-36	74.5	25.5	0	
4-37	75.2	24.8	0.01	
4-38	75.6	24.2	0.16	
4-39	74.5	24.8	0.77	
4-40	73.8	25.9	1.27	
4-41	72.2	25.2	2.67	
4-42	71.5	25.8	2.69	
4-43	70.5	26.4	3.09	liquid+dicalcium ferrite+
4-44	69.5	27.1	3.37	dicalcium silicate
4-45	76.8	20.2	2.98	liquid+spinel+
				dicalcium silicate

The liquidus points in the Fe_3O_4 corner of Fe_3O_4 –CaO– SiO_2 system were determined at $p\text{O}_2$ of 10^{-6} under varying temperature and the results are shown in Fig. 9. It is noted that the liquidus lines at 1623 and 1673 K protrude toward the composition of wollastonite ($\text{CaO}\cdot\text{SiO}_2$). It is shown in Fig. 9(c) that the stable region of spinel decreases drastically with increasing temperature.

Table 5 Composition (mass%) of Fe_3O_4 –CaO– SiO_2 slag at 1573 K and $p\text{O}_2$ of 10^{-7} .

No.	Fe_3O_4	CaO	SiO_2	Phases
5-1	67.8	3.77	28.5	liquid
5-2	67.6	3.69	28.7	
5-3	46.8	21.2	32.0	
5-4	67.8	0	32.2	liquid+tridimite
5-5	67.2	0	32.8	
5-6	50.1	26.7	23.1	liquid+spinel
5-7	76.1	0	23.9	
5-8	48.2	26.1	25.7	
5-9	60.7	12.2	27.1	
5-10	64.1	8.16	27.8	
5-11	48.8	22.0	29.2	
5-12	58.2	12.3	29.5	
5-13	54.0	16.4	29.6	
5-14	54.1	16.3	29.6	

Table 6 Composition (mass%) of Fe_3O_4 –CaO– SiO_2 slag at 1573 K and $p\text{O}_2$ of 10^{-5} .

No.	Fe_3O_4	CaO	SiO_2	Phases
6-1	33.2	32.8	34.0	liquid
6-2	30.1	35.1	34.8	
6-3	40.1	26.6	33.3	liquid+spinel
6-4	34.8	31.6	33.6	
6-5	43.1	22.7	34.2	
6-6	42.8	22.6	34.6	
6-7	60.9	4.23	34.8	
6-8	55.9	9.02	35.1	
6-9	60.6	4.31	35.1	
6-10	48.0	16.4	35.6	
6-11	47.6	16.1	36.4	
6-12	52.6	10.5	36.8	
6-13	64.1	2.10	33.8	liquid+spinel+tridimite
6-14	63.3	2.79	33.9	

Table 7 Composition (mass%) of Fe_3O_4 –CaO– SiO_2 slag at 1573 K and $p\text{O}_2$ of 3.63×10^{-4} .

No.	Fe_3O_4	CaO	SiO_2	Phases
7-1	46.1	17.3	36.6	liquid+spinel
7-2	48.0	15.3	36.7	
7-3	39.3	23.6	37.1	
7-4	45.3	17.6	37.1	
7-5	50.1	11.4	38.5	
7-6	43.4	17.9	38.7	
7-7	28.4	31.5	40.1	
7-8	18.9	40.7	40.4	
7-9	18.7	40.0	41.3	
7-10	16.7	41.0	42.3	
7-11	52.1	10.4	37.5	liquid+spinel+tridimite

Table 8 Composition (mass%) of Fe_3O_4 – CaO – SiO_2 slag at 1623 K and $p\text{O}_2$ of 10^{-6} .

No.	Fe_3O_4	CaO	SiO_2	Phases
8-1	83.4	16.3	0.27	liquid+spinel
8-2	81.3	15.6	3.06	
8-3	48.9	29.9	21.3	
8-4	73.7	0	26.3	
8-5	43.9	29.4	26.7	
8-6	48.7	23.3	28.0	
8-7	56.0	14.1	29.9	
8-8	61.0	8.78	30.2	

Table 9 Composition (mass%) of Fe_3O_4 – CaO – SiO_2 slag at 1673 K and $p\text{O}_2$ of 10^{-6} .

No.	Fe_3O_4	CaO	SiO_2	Phases
9-1	78.8	21.2	0	liquid
9-2	83.3	14.0	2.75	
9-3	85.7	11.1	3.24	
9-4	84.2	9.88	5.90	
9-5	78.2	11.9	9.90	
9-6	80.0	4.05	16.0	
9-7	82.8	0	17.2	
9-8	59.8	21.8	18.5	
9-9	63.4	17.1	19.5	
9-10	54.6	22.2	23.1	
9-11	66.7	10.1	23.2	
9-12	65.8	6.94	27.3	
9-13	64.2	4.38	31.4	
9-14	34.5	32.7	32.8	
9-15	28.7	25.5	45.8	
9-16	91.8	7.95	0.31	liquid+spinel
9-17	91.4	7.66	0.93	
9-18	92.1	6.50	1.38	
9-19	80.6	10.4	8.99	
9-20	81.5	9.20	9.33	
9-21	79.8	9.29	10.9	
9-22	88.9	0.01	11.1	
9-23	84.4	3.05	12.5	
9-24	81.0	6.19	12.9	
9-25	83.2	3.46	13.3	

The liquidus composition on the SiO_2 side in the FeO – SiO_2 system reported by Muan *et al.*¹⁰⁾ at $p\text{O}_2$ of 10^{-7} and 1573 K and at $p\text{O}_2$ of 10^{-6} and 1673 K agrees well with the present results, while that on the FeO side reported by the same authors¹⁰⁾ is systematically 3~5 mass% smaller than the present results. The reported liquidus composition in the Fe_3O_4 side in the Fe_3O_4 – CaO – SiO_2 system at 1573 K and $p\text{O}_2$ of 10^{-7} reported by Shigaki *et al.*⁵⁾ is at variance with the

Fig. 4 Phase diagram of FeO – CaO – SiO_2 slag at 1573 K and $p\text{O}_2$ of 10^{-8} (stable iron oxide: “FeO”). Fig. 5 Comparison of homogenous liquid region between the slags at 1573 K and $p\text{O}_2$ of 10^{-8} and iron saturation (stable iron oxide: “FeO”). Fig. 6 Liquidus in the “FeO” corner of FeO – CaO – SiO_2 slag at 1573 K (stable iron oxide: “FeO”).

Fig. 7 Phase diagram of Fe_3O_4 -CaO-SiO₂ slag at 1573 K and $p\text{O}_2$ of 10^{-6} (stable iron oxide: Fe_3O_4).

present results. Also, the liquid regions reported by Kimura *et al.*⁶⁾ at 1573 K and $p\text{O}_2$ of 1.8×10^{-6} and 1.8×10^{-8} , which are extended as a continuum from the SiO₂-free FeO_x -CaO system until around 55 mass% silica, disagree with the present results.

3.3 Comparison of homogeneous liquid region at 1573 K

The liquid regions at the oxygen partial pressures of 10^{-8} and 10^{-6} , which were determined in this study, and those reported by Phillips *et al.*¹²⁾ in air at 1573 K are illustrated in Fig. 10. Although the systems at $p\text{O}_2$ of 10^{-8} and 10^{-6} form FeO and Fe_3O_4 in the iron-rich corner, respectively, a congruently proportional transition is observed where the

increase in the oxygen partial pressure has an effect to reduce the liquid area in the iron-rich corner and also to stabilize tridimite, wollastonite, dicalcium silicate and dicalcium ferrite. The effect of the transition between spinel and hematite is more remarkable, as indicated by the difference in the slope of liquidus line in the FeO_x corner, the displacement of the liquid region in air to the Fe_2O_3 -CaO axis and the increasing liquid region in air in the lower portion of the diagram.

3.4 Considerations for practical operation

It is considered from the present experimental results that a metallurgical process with the FeO_x -CaO-SiO₂ slags at 1573 K will be easily encountered with a problem of magnetite precipitation when the partial pressure of oxygen exceeds 10^{-7} because the homogeneous liquid area is remarkably reduced in the region of higher oxygen pressure, as shown in Fig. 10. However, as shown in Fig. 8(d), the precipitation of iron oxide (wüstite or spinel) at 1573 K and the oxygen partial pressure between 10^{-8} and 10^{-7} will not be so sensitive to the variation of the oxygen pressure. Although, as shown in Fig. 4, the FeO -CaO-SiO₂ slag at 1573 K and $p\text{O}_2$ of 10^{-8} represents a considerably wide liquid region, the liquidus line in the FeO corner remarkably protrudes along the composition line with the mass% ratio of CaO/SiO₂ around 1. This suggests that careful control of the slag composition should be made to avoid the problem of solid precipitation when the process is operated with the slag of CaO/SiO₂ ratio around 1.

Since the slag in metallurgical operations commonly

Fig. 8 Phase diagram of Fe_3O_4 -CaO-SiO₂ slag at 1573 K and $p\text{O}_2$ of 3.63×10^{-4} to 10^{-7} (stable iron oxide: Fe_3O_4).

Fig. 9 Phase diagram of Fe_3O_4 – CaO – SiO_2 slag from 1573 to 1673 K and p_{O_2} of 10^{-6} (stable iron oxide: Fe_3O_4).

contain considerable amounts of minor components such as Cu_2O , Al_2O_3 and MgO , which will more or less increase or reduce the homogeneous liquid region, a further study is required on the effect of these components on the liquidus lines in the FeO_X – CaO – SiO_2 base slags.

4. Conclusions

The phase relations in the FeO – CaO – SiO_2 and Fe_3O_4 – CaO – SiO_2 slags at 1573–1673 K and the intermediate oxygen partial pressures between 10^{-9} and 3.63×10^{-4} were investigated by a quenching method combined with

Fig. 10 Homogeneous liquid region of FeO_X – CaO – SiO_2 slag at 1573 K.

EPMA analysis of the liquid and solid phases using a crucible of platinum foil. The results were compared with those obtained at the iron saturation and in equilibrium with air. As a general tendency, the homogeneous liquid area decreased with increasing oxygen partial pressure. For the liquidus saturated with spinel at 1573 K, decreasing the oxygen partial pressure from 3.63×10^{-4} to 10^{-6} resulted in a displacement of the liquidus line to the FeO_X – SiO_2 side without any appreciable extension of the liquid area. However, by increasing the temperature up to 1673 K, the stable region of spinel was remarkably reduced. At 1573 K, in the range of oxygen partial pressures where wüstite appears, increase in the oxygen partial pressure had a large effect on the stable region of wüstite. In contrast with the FeO – CaO – SiO_2 system, in the range of oxygen partial pressures between 10^{-6} and 3.63×10^{-4} in the Fe_3O_4 – CaO – SiO_2 at 1573 K, increasing the oxygen partial pressure apparently had a weak effect on the stable region of spinel.

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