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LIQUIDUS AND PHASE EQUILIBRIA IN CaO-Al_2O_3-FeO_X-SiO_2 SYSTEM UNDER INTERMEDIATE OXYGEN PARTIAL PRESSURE

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Abstract

Liquidus and phase equilibria in CaO-Al_2O_3-FeO_x and CaO-Al_2O_3-FeO_x-SiO_2 systems under intermediate oxygen partial pressures of 10.13Pa and 1.01×10^{-1}Pa have been experimentally investigated, by means of high temperature equilibration, quenching technique, Scanning Electronic Microscope with Energy Dispersive Spectrometer (SEM-EDS), and X-ray Diffraction (XRD). For CaO-Al_2O_3-FeO_x system, both two-phase coexistence and three-phase coexistence, including liquid, $CaAl_2O_4$, $CaAl_4O_7$ and spinel, are observed in high Al_2O_3 zone at mentioned oxygen partial pressures, but the equilibrated phases at at 1450 °C are a little different from those at 1550 °C. With addition of 10mass% SiO_2, melilite phase was found around the primary phase field of $CaAl_4O$ in CaO-Al_2O_3-FeO_x-SiO_2 system. The liquidus data around the boundaries of $CaAl_2O_4$ and $CaAl_4O_7$ primary phase fields in CaO-Al_2O_3-FeO_x system are obtained under the two intermediate oxygen partial pressures, and the effect of oxygen partial pressure on the liquidus has been discussed.

Keywords: *CaO-Al_2O_3-FeO_x-SiO_2 system; Liquidus; Phase equilibria; Intermediate oxygen partial pressure.*

1. Introduction

CaO-Al_2O_3-FeO_x and CaO-Al_2O_3-FeO_x-SiO_2 systems are significant in the processes of ferrous and non-ferrous metals production. They are also the primary sub-systems of CaO-SiO_2-Al_2O_3-MgO-FeO_x-Na_2O multi-component oxide system, which as known can be formed during the vitrification of municipal solid waste incineration ash [1]. The thermodynamic information of CaO-Al_2O_3-FeO_x and CaO-Al_2O_3-FeO_x-SiO_2 systems, such as liquidus and phase equilibria, would be helpful for ash-treatment in molten phase with an environmental-friendly manner [2]. They are also useful for the utilization of lower grade mineral materials in metallurgical industries, due to the problem of natural resource depleting [3-4]. Literature review showed that the investigations on CaO-Al_2O_3-FeO_x and CaO-Al_2O_3-FeO_x-SiO_2 systems are almost restricted to Fe_2O_3-containing systems with higher oxygen partial pressure and those equilibrium with iron, so just a few experimental studies on the phase equilibria and liquidus at intermediate oxygen partial pressures are available [5-9]. In the present work, liquidus and phase relations for CaO-Al_2O_3-FeO_x and CaO-Al_2O_3-FeO_x-SiO_2 systems under intermediate oxygen partial pressures of 10.13Pa and 1.01×10^{-1}Pa, have been experimentally examined with equilibrium testing, SEM-EDS and XRD measurements. The experimental results would contribute to the thermodynamic properties modeling of the two oxide systems and multi-component oxide system, which is required for the construction of the relevant phase diagrams.

2. Experimental

Experimental procedure is given in three parts – sample preparation, temperature and gas atmosphere control, equilibrium experiments, in accordance to the details already presented in Ref.[9].

2.1 Sample preparation

Laboratory reagent grade powders of CaO, Al_2O_3, SiO_2, and $C_2FeO_4\cdot2H_2O$ with purity level of 99.5% were used for slag synthesis. ($C_2FeO_4\cdot2H_2O$ at 600 °C for 2h). These mixtures were accurately weighed in the required proportions and then ground and mixed

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well in an agate mortar. Subsequently, the mixtures were pressed into a tablet as slag sample. The above procedures minimize the heterogeneity of the mixture sample and promote the phase transformation and melting of the mixture. In the following, the prepared slag sample, wrapped in platinum foil, was charged in an alumina crucible and placed in the constant temperature zone of an electrical resistance tube furnace.

2.2 Temperature and gas atmosphere control

Sample temperature was measured with a Pt-Rh30/Pt-Rh6 thermocouple with an accuracy of ±2°C. The atmosphere within the furnace was controlled at a fixed oxygen partial pressure by using H_2/CO_2 gas mixtures on the basis of the equilibrium of reactions (1) and (2) [10]. The thermodynamic oxygen partial pressures for different ratios of H_2/CO_2 gas mixtures are shown in Table 1, which were verified with the measurements of a mass spectrograph with the results shown also in Table 1. Flow rates of gas mixture were controlled using mass flow controller with the gas flowing from the bottom to the top of the furnace. A high purity CO_2 gas was purified by H_2SO_4 and $Mg(ClO_4)_2$, and a high purity H_2 gas was purified by silica gel and P_2O_5.

$$2CO_2(g)=2CO(g)+O_2(g) \quad ...(1)$$

$$\Delta G^O(1)= 564300 -173.4T \quad J\cdot mol^{-1}$$

$$H_2(g)+CO_2(g)=H_2O(g)+CO(g) \quad ...(2)$$

$$\Delta G^O(2)= 77205 -64.12T \quad J\cdot mol^{-1}$$

Table 1. *Thermodynamic oxygen partial pressure at specified temperature*

Temperature (°C)	Gas Mixture P_{H2}/P_{CO2}	Target P_{O2} (Pa)	Measured P_{O2} (Pa)
1450	0.01	10.13	10.89
1450	0.09	1.01×10^{-1}	0.81×10^{-1}
1550	0.03	10.13	8.94
1550	0.23	1.01×10^{-1}	1.36×10^{-1}

2.3 Equilibration experiments

The experimental mixture compositions were selected, that would result in the formation of one or two condensed phases at the equilibrium temperature. From the experimental results, the liquidus and phase relations at intermediate oxygen partial pressure could be investigated and determined.

For each experimental round, the sample was firstly held at 600°C for 2 hours under argon atmosphere to decarburize $C_2FeO_4\cdot 2H_2O$. Then the sample was pre-melted at a temperature of 20°C to 30°C higher than the melting point, to ensure the formation of homogeneous melting. The premelting period lasted 3 hours under flowing Ar atmosphere. Subsequently, the gas mixtures were adjusted to the required oxygen partial pressure, and the samples were equilibrated at the specified equilibrium temperature for 24~48 hours. The sample was rapidly taken out from the furnace and quenched in an argon gas flow, after the equilibrium.

Quenched samples were embedded in epoxy resin and polished subsequently. SEM-EDS were applied for structural analysis and identification of equilibrium phases in the quenched samples. X-ray powder diffraction (XRD) analysis was used in some cases to confirm the phase identification suggested by the EDS analysis.

3. Results and Discussion

3.1 Phase equilibria of the quenched slag samples

The equilibrium phases for $CaO-Al_2O_3-FeO_x$ system at the oxygen partial pressures of 10.13Pa and 1.01×10^{-1}Pa are shown in Table 2 and Table 3 respectively. The corresponding experimental results for $CaO-Al_2O_3-FeO_x-SiO_2$ system are presented in Table 4. The compositions of liquid and condensed phases were analyzed by EDS.

Figure 1 and Figure 2 are the typical back-scattered scanning electron microscope (SEM) micrographs for the quenched $CaO-Al_2O_3-FeO_x$ system slag samples involving liquid and the equilibrated solid phase(s) with 10.13Pa and 1.01×10^{-1}Pa oxygen partial pressures, respectively. Figure 3 shows the equilibrated phases of samples 6 and 7 identified by XRD. Figure 4 gives the SEM micrograph and XRD pattern of the quenched slag sample of $CaO-Al_2O_3-FeO_x-SiO_2$ system with 10.13Pa oxygen partial pressure. For $CaO-Al_2O_3-FeO_x$ system, the phase equilibrium contain two cases, i.e. the two-phase coexistence and the three-phase coexistence in high Al_2O_3 content zone. The two-phase coexistence contains liquid (L) in equilibrium with $CaAl_4O_7(CA_2)/CaAl_2O_4(CA)$ at either 1450°C or 1550°C. On the other hand, the three-phase coexistence contains liquid (L), $CaAl_2O_4(CA)$ and $CaAl_4O_7(CA_2)$ at 1450°C, while the equilibrium phases are liquid (L), $CaAl_4O_7(CA_2)$ and Spinel(Sp) at 1550°C. For $CaO-Al_2O_3-FeO_x-10\%SiO_2$ system under the oxygen partial pressure of 10.13Pa, melilite phase was found around the primary phase field of $CaAl_4O_7$, and the three-phase coexistence are liquid (L), $CaAl_4O_7(CA_2)$ and melilite(Me) equilibrated at 1450°C.

Table 2. *Equilibrium phase compositions of CaO-Al_2O_3-FeO_x system with P_{O_2}= 10.13Pa*

Sample	Temperature (°C)	Original Composition (mass%)			Phases after Equilibrium	Composition after Equilibrium (mass%)		
		Al_2O_3	CaO	FeO_x		Al_2O_3	CaO	FeO_x
1	1450	45.77	23.59	30.64	Liquid	32.4	24.27	43.33
					$CaO\cdot 2Al_2O_3$	74.92	23.85	1.23
2	1450	55.65	27.04	17.31	Liquid	23.78	16.54	59.68
					$CaO\cdot 2Al_2O_3$	74.37	21.44	4.19
3	1450	51.5	40.25	8.25	Liquid	28.72	15.72	55.56
					$CaO\cdot 2Al_2O_3$	77.71	19.85	2.44
4	1450	48.01	26.15	25.84	Liquid	46.33	31.17	22.5
					$CaO\cdot Al_2O_3$	58.66	39.91	1.43
					$CaO\cdot 2Al_2O_3$	73.61	25.48	0.91
5	1450	51.47	19.35	29.17	Liquid	43.83	42.91	13.26
					$CaO\cdot Al_2O_3$	62.83	35.86	1.31
6	1450	49.03	20.73	30.24	Liquid	37.92	28.6	33.48
					$CaO\cdot Al_2O_3$	58.73	37.29	3.98
					$CaO\cdot 2Al_2O_3$	73.81	23.86	2.33
7	1550	54.19	22.69	23.12	Liquid	40.09	14.05	45.86
					$CaO\cdot 2Al_2O_3$	74.76	22.51	2.73
					Spinel	58.45	0.77	40.78
8	1550	62.63	29.32	8.05	Liquid	45.16	23.39	31.45
					$CaO\cdot Al_2O_3$	72.82	25.77	1.41
9	1550	51.2	18.42	30.38	Liquid	48.23	28.87	22.9
					$CaO\cdot 2Al_2O_3$	71.38	24.43	4.19
10	1550	57.3	26.89	15.81	Liquid	57.43	32.97	9.6
					$CaO\cdot Al_2O_3$	62.38	36.25	1.37
					$CaO\cdot 2Al_2O_3$	76	21.65	2.35

Table 3. *Equilibrium phase compositions of CaO-Al_2O_3-FeO_x system with P_{O_2}= 1.01×10^{-1}Pa*

Sample	Temperature (°C)	Original Composition (mass%)			Phases after Equilibrium	Composition after Equilibrium (mass%)		
		Al_2O_3	CaO	FeO_x		Al_2O_3	CaO	FeO_x
11	1450	51.13	19.63	29.24	Liquid	29.55	11.99	58.46
					$CaO\cdot 2Al_2O_3$	77.05	18.56	4.4
12	1450	48.72	21.33	29.95	Liquid	34.75	18.69	46.56
					$CaO\cdot 2Al_2O_3$	76.22	20.6	3.08
13	1450	48.76	25.82	25.42	Liquid	41.2	23.44	35.36
					$CaO\cdot 2Al_2O_3$	75.98	19.54	4.48
14	1550	53.08	17.97	28.95	Liquid	44.99	17.17	37.84
					Spinel	53.74	1.48	44.78
					$CaO\cdot 2Al_2O_3$	75.35	22.7	1.95
15	1550	55.83	22.97	21.2	Liquid	49.67	25.22	25.11
					$CaO\cdot 2Al_2O_3$	75.72	20.96	3.32

Table 4. *Equilibrium phase compositions of CaO-*Al_2O_3*-*FeO_x*-*SiO_2 *system with* P_{O_2}*= 10.13Pa*

Sample	Temperature (°C)	Original Composition (mass%)				Phases after Equilibrium	Composition after Equilibrium (mass%)			
		Al_2O_3	CaO	FeO_x	SiO_2		Al_2O_3	CaO	FeO_x	SiO_2
16	1450	36.5	40.9	12.6	10	Liquid	32.54	13.49	21.43	32.54
						Melilite	24.84	49.94	0.38	24.84
17	1450	33.8	33.8	22.4	10	Liquid	30.5	25.27	34.84	9.4
						Melilite	39.63	37.69	0.2	22.48
						$CaO\cdot 2Al_2O_3$	70.15	20.16	0.51	1.33
18	1450	40.8	28.7	20.5	10	Liquid	32.94	25.39	32.67	9
						Melilite	34.28	45.81	0.32	19.59
						$CaO\cdot 2Al_2O_3$	75.13	23.13	1.38	0.36

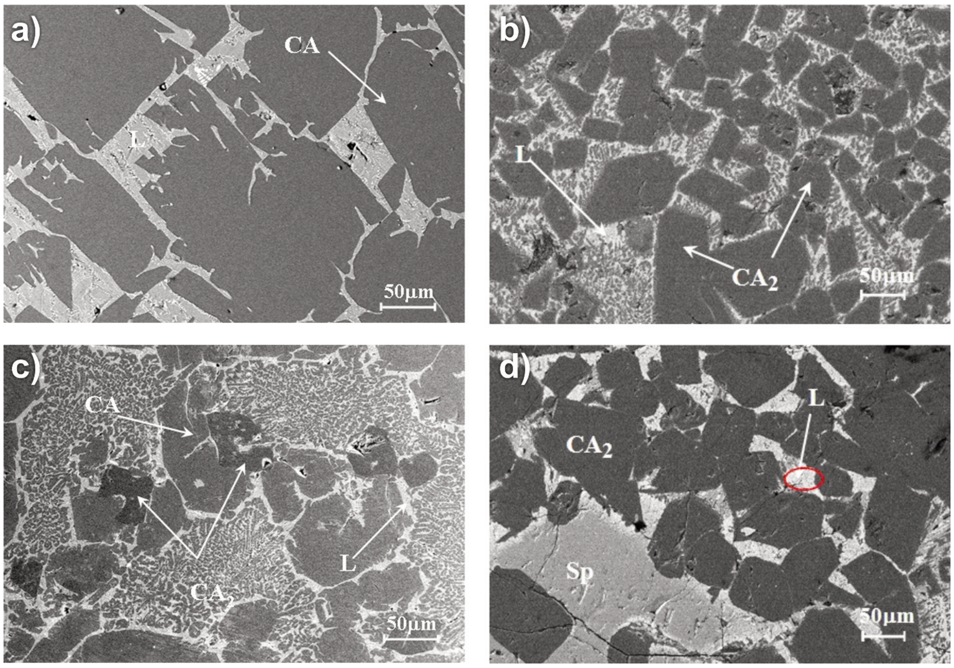

Figure1. *Backscattered SEM micrographs of equilibrated CaO-*Al_2O_3*-*FeO_x *slag samples with* P_{O_2}*= 10.13Pa, (a) L and CA in sample 5 equilibrated at 1450°C, (b) L and* CA_2 *in sample 9 equilibrated at 1550°C, (c) L, CA and* CA_2 *in sample 6 equilibrated at 1450°C, (d) L,* CA_2 *and Sp in sample 7 equilibrated at 1550°C*

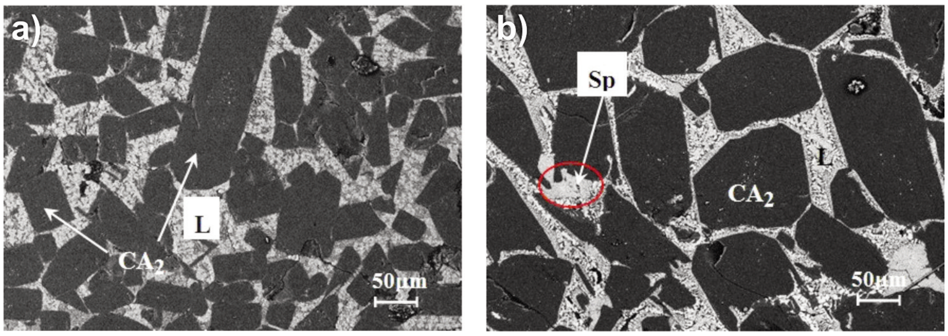

Figure 2. *Backscattered SEM micrographs of equilibrated CaO-*Al_2O_3*-*FeO_x *slag samples with* P_{O_2}*= 1.01´*10^{-1}*Pa, (a) L and* CA_2 *in sample 12 equilibrated at 1550°C, (b) L,* CA_2 *and Sp in sample 14 equilibrated at 1550°C*

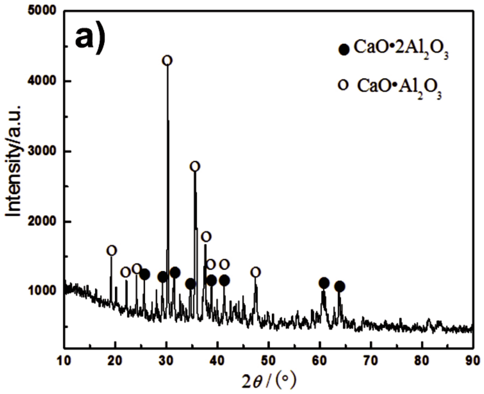

Figure 3. *XRD patterns of the quenched samples 6 and 7 from CaO-*Al_2O_3*-*FeO_x *system with* P_{O_2}*= 10.13Pa, (a) Sample 6 equilibrated at 1450°C, (b) Sample 7 equilibrated at 1550°C*

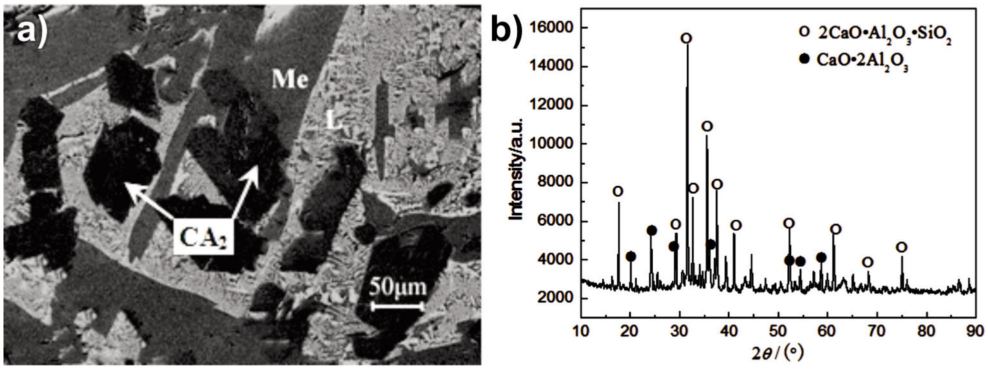

Figure 4. *Equilibrated phases of CaO-*Al_2O_3*-*FeO_x*-*SiO_2 *system with* P_{O_2}*= 10.13Pa, (a) L,* CA_2 *and Me in sample 18 equilibrated at 1450°C, (b) XRD pattern of sample 18 at 1450°C*

3.2Liquidus of CaO-Al_2O_3*-*FeO_x *system under intermediate oxygen partial pressure*

Figure 5 shows the variation of liquidus in CaO-Al_2O_3-FeO_x system under different intermediate oxygen partial pressures, in which (a) is at 1450°C and (b) is at 1550 °C. The experimental liquidus are shown as dot marks, while the predicted liquidus by FactSage are presented by dash and solid lines [11].

With the decrease of from 10.13Pa to 1.013×10^{-1}Pa, the liquid zone expands and the liquidus around the primary phase fields of CaO·Al_2O_3 and CaO·$2Al_2O_3$ shift to the FeO_x-Al_2O_3 side, which indicating that the liquid forms more easily with higher FeO_x content at lower oxygen partial pressure. At 1450 °C, the liquidus of CaO·$2Al_2O_3$ primary phase field was lifted to the FeO_x rich region with the decrease of oxygen partial pressure. On the other hand, at either 1450°C or 1550°C, no appreciable effect of oxygen partial pressure on the liquidus of

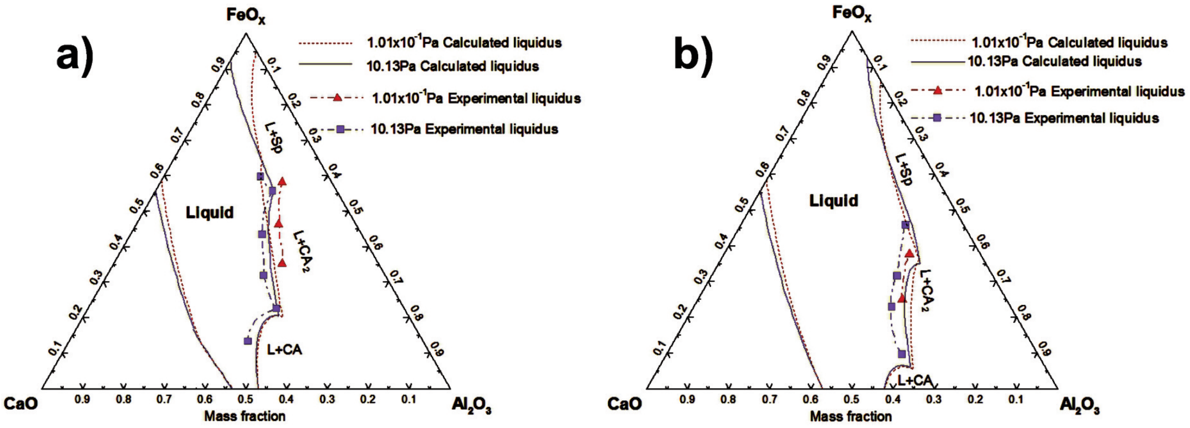

Figure 5. *Liquidus of CaO-*Al_2O_3*-*FeO_x *system under intermediate oxygen partial pressure, (a) at 1450°C, (b) at 1550°C*

$CaO{\cdot}Al_2O_3$ primary phase field can be noted. However, experimental results are in good agreement with liquidus calculated by FactSage.

4. Conclusions

Equilibrium phase relations in $CaO\text{-}Al_2O_3\text{-}FeO_x$ system were confirmed under 10.13Pa and 1.01×10^{-1}Pa intermediate oxygen partial pressures, and the spinel was found in the primary field of $CaO{\cdot}2Al_2O_3$. Liquidus data was reported around the primary phase fields of $CaO{\cdot}Al_2O_3$ and $CaO{\cdot}2Al_2O_3$ under 10.13Pa or 1.01×10^{-1}Pa oxygen partial pressures, which contribute to the thermodynamic properties modeling of the relevant multi-component oxide system. With the decrease of oxygen partial pressure, the liquid area expands and shifts to the $FeO_x\text{-}Al_2O_3$ side, especially along the primary phase field of $CaO{\cdot}2Al_2O_3$. With the addition of 10%SiO_2, melilite phase is found in $CaO\text{-}Al_2O_3\text{-}FeO_x\text{-}10\%SiO_2$ system, and the three-phase coexistence are liquid (L), $CaAl_4O_7$(CA_2) and melilite(Me) equilibrated at 1450°C.

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