Liquidus and phase equilibria in CaO-SiO_2-FeO_x-Al_2O_3 system under intermediate oxygen partial pressure

Nan WANG1), Shuichao CHEN1), Zongshu ZOU1), Zhan ZHANG2), Yanping XIAO2) and Yongxiang YANG2)*

1) School of Materials & Metallurgy, Northeastern University, 110819, China

2) Dept. of Materials Science and Engineering, Delft University of Technology, 2628 CD, The Netherlands

Abstract: The thermodynamic information of CaO-Al_2O_3-FeO_x and SiO_2-Al_2O_3-FeO_x systems are necessary for the design of metallurgical process and analysis of the vitrified bottom ash slag from municipal solid waste incineration ash. High temperature equilibrium experiments were carried out to investigate the effects of temperature on the equilibrium phase relations and liquidus lines for both CaO-Al_2O_3-FeO_x and SiO_2-Al_2O_3-FeO_x systems at intermediate oxygen partial pressure of 10^{-4} atm. The experimental results by employing Electron Probe MicroAnalysis (EPMA) and Scanning Electron Microscope (SEM) analysis method showed an appreciable effect of temperature on the phase relations and liquidus. For CaO-Al_2O_3-FeO_x system, both two-phase coexistence and three-phase coexistence regions are observed at either 1450°C or 1550°C, but the equilibrated phases in the two-phase region are different for the two temperatures. The liquid area of CaO-Al_2O_3-FeO_x system enlarges and the liquidus on the Al_2O_3-FeO_x side moves to the high Al_2O_3 region from 1450°C to 1550°C. For SiO_2-Al_2O_3-FeO_x system, only two-phase region is found at 1550°C, and the liquid area enlarges to the high iron oxide region as well as to the primary phase field of mullite with rising the temperature. The present experimental results on the liquidus showed a good agreement with the FactSage predictions.

Keywords: CaO-Al_2O_3-FeO_x system, SiO_2-Al_2O_3-FeO_x system, liquidus, phase relations, intermediate oxygen partial pressure

1. Introduction (10 pt bold Times New Roman)

CaO-Al_2O_3-FeO_x and SiO_2-Al_2O_3-FeO_x ternaries are important systems 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 SiO_2-Al_2O_3-FeO_x systems, such as the liquidus lines and phase relations, 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， which have to be used due to the superior natural resource depleting. Through literature survey, it is found that the investigations on CaO-Al_2O_3-FeO_x and SiO_2-Al_2O_3-FeO_x ternaries are restricted to Fe_2O_3-containing systems with higher oxygen partial pressure. Dayal and Galsser studied the liquidus surface in the CaO-Al_2O_3-FeO_x system in air by the quenching technique, and only two-phase regions were observed experimentally. In addition, isothermal sections through the system at 1145°C in air were also studied by those authors [3]. Muan studied the liquidus and solidus surface in air and liquidus relations for Al_2O_3-FeO_x-SiO_2 system under the oxygen partial pressure of 1 atm [4]. Therefore, knowledge of liquidus temperatures and phase relations at equilibrium for the above two systems at various oxygen partial pressure is also required, especially for the systematic process optimization and design of metallurgy as well as the solid waste recycling and utilization.

In the present work, liquidus lines and phase relations for $CaO-Al_2O_3-FeO_x$ and $SiO_2-Al_2O_3-FeO_x$ systems under intermediate oxygen partial pressure of 10^{-4} atm at 1450°C and 1550°C, have been experimentally examined by means of high temperature equilibration technique, Electron Probe MicroAnalysis (EPMA), and Scanning Electron Microscope (SEM). The experimental results would contribute to the thermodynamic property modeling of the two ternaries and multi-component oxide system， which is required for the construction of the relevant phase diagrams.

2. Experimental

2.1 Sample preparation

Starting oxide mixtures were made from reagent grade chemical powders of SiO_2 (99.7 wt%), Al_2O_3 (99.7 wt%), CaO (calcined from 99.9 wt% $CaCO_3$ powder), and iron oxide (prepared by calcining ($C_2FeO_4\cdot 2H_2O$ at 600℃ for 2h). These mixtures were accurately weighed carefully in the required molar ratios and mixed in an agate mortar and pestled for 30 minutes, and then pressed with a pressure of 30 MPa to produce a tablet (20g). The tablet was subsequently being broken to the required shape and wrapped in a platinum foil. The wrapped sample was placed inside an open aluminum crucible, and positioned in the even temperature zone of the Al_2O_3 vertical tube (100mm i.d. , 110 mm o. d. and 900mm in height) of an electrical resistance furnace with MoS_2 as heating unit for equilibrium experiments.

2.2 Temperature and gas atmosphere control

The furnace temperature was monitored by a Pt-Rh30/Pt-Rh6 thermocouple, and the temperature of the sample was also measured with a Pt-Rh30/Pt-Rh6 thermocouple placed next to it with an temperature accuracy of ±2°C. The even temperature zone of the furnace was about 100mm. 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 the reactions (1) and (2) [5]). The oxygen partial pressures for different ratios of H_2/CO_2 gas mixtures are shown in Table 1. Flow rates of gases to the furnace with 1000 ml/min, 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.

$$2CO_2(g)=2CO(g)+O_2(g) \tag{1}$$

$$\triangle G^0= 564300 -173.4T \quad J\cdot mol^{-1}$$

$$H_2(g)+CO_2(g)=H_2O(g)+CO(g) \tag{2}$$

$$\triangle G^0= 77205 -64.12T \quad J\cdot mol^{-1}$$

Table 1 Thermodynamic oxygen partial pressure at specified temperature

Equilibrium temperature (℃)	Gas mixture	Log(P_{O_2}) (atm)
1450	H_2/CO_2=0.00937	-4.0
1550	H_2/CO_2=0.02781	-4.0

2.3 Equilibration experiments

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

Firstly, all samples were pre-melted at a temperature of 20°C to 30°C higher than the melting point to ensure the formation of homogeneous melting, and the premelting period lasted 2 hours under flowing Ar atmosphere. Subsequently, the gas mixtures were adjusted to maintain the required oxygen partial pressure, and the samples were equilibrated at the specified equilibrium temperature for 24 hours. After the equilibrium, the sample was rapidly taken out from the furnace and quenched in an argon gas flow.

The quenched samples were embedded in epoxy resin and polished subsequently. SEM and EPMA were employed for microstructural and compositional analysis for identifying the phases in the equilibrium in the quenched samples.

3. Results and discussion

3.1 Phases of the quenched slag samples

The equilibrium for CaO-Al_2O_3-FeO_x system at the oxygen partial pressure of 10^{-4} atm has been achieved at 1450 and 1550℃ respectively, the results are shown in Table 2. The corresponding results for SiO_2-Al_2O_3-FeO_x system are shown in Table 3. The compositions of liquid and condensed phases were determined using EPMA.

Table 2 Experiment results of CaO-Al_2O_3- FeO_x system

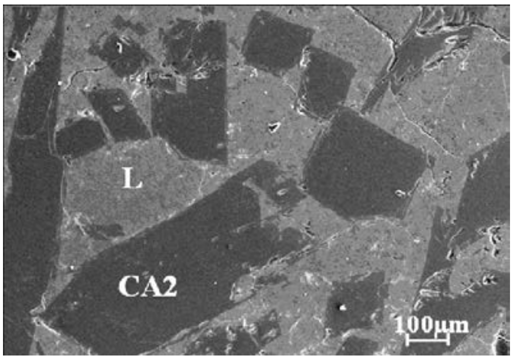
Sample	Temperature (℃)	Weighted-in compositions (mass%)			Phase in equilibrium	Analyzed compositions (mass%)		
		Al_2O_3	CaO	FeO_x		Al_2O_3		CaO
						FeO_x		
1	1450	45.77	23.59	30.64	Liquid	32.40	24.27	43.33
					$CaO·2Al_2O_3$	74.92	23.85	1.23
2	1450	55.65	27.04	17.31	Liquid	46.33	31.17	22.50
					$CaO·Al_2O_3$	58.66	39.91	1.43
					$CaO·2Al_2O_3$	73.61	25.48	0.91
3	1450	51.50	40.25	8.25	Liquid	45.67	42.50	11.83
					$CaO·Al_2O_3$	62.83	35.86	1.31
4	1450	48.01	26.15	25.84	Liquid	37.92	28.60	33.48
					$CaO·Al_2O_3$	60.50	38.42	1.08
5	1550	54.19	22.69	23.12	Liquid	46.07	23.01	30.92
					$CaO·Al_2O_3$	72.82	25.77	1.41
6	1550	62.63	29.32	8.05	Liquid	57.43	32.97	9.60
					$CaO·Al_2O_3$	62.38	36.25	1.37
					$CaO·2Al_2O_3$	76.00	21.65	2.35

Table 3 Experiment results of SiO_2-Al_2O_3-FeO_x system

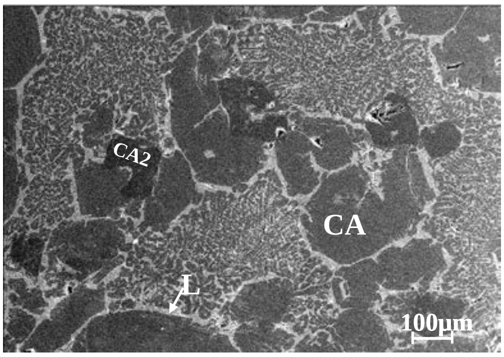
Sample	Temperature (℃)	Weighted-in compositions (mass%)			Phase in equilibrium	Analyzed compositions (mass%)		
		Al_2O_3	SiO_2	FeO_x		Al_2O_3		SiO_2
						FeO_x		
1	1450	35.00	35.30	29.7	Liquid	25.12	37.01	37.86

					Mullite	65.55	26.51	7.94
2	1450	30.30	46.90	22.80	Liquid	20.66	59.30	20.04
					Mullite	64.63	28.81	6.56
3	1450	24.40	57.80	17.80	Liquid	17.71	65.55	16.74
					Mullite	17.10	62.67	20.23
4	1450	20.40	64.00	15.60	Liquid	16.25	62.00	21.75
					SiO_2	0.10	99.70	0.20
					Mullite	67.08	32.02	0.90
5	1550	32.54	44.56	22.90	Liquid	29.36	45.96	24.68
					Mullite	66.48	28.75	4.77
6	1550	38.62	35.6	25.78	Liquid	28.81	38.00	33.19
					Mullite	66.11	26.66	7.23
7	1550	41.70	30.10	28.20	Liquid	35.50	30.70	33.80
					Mullite	63.09	26.77	10.15

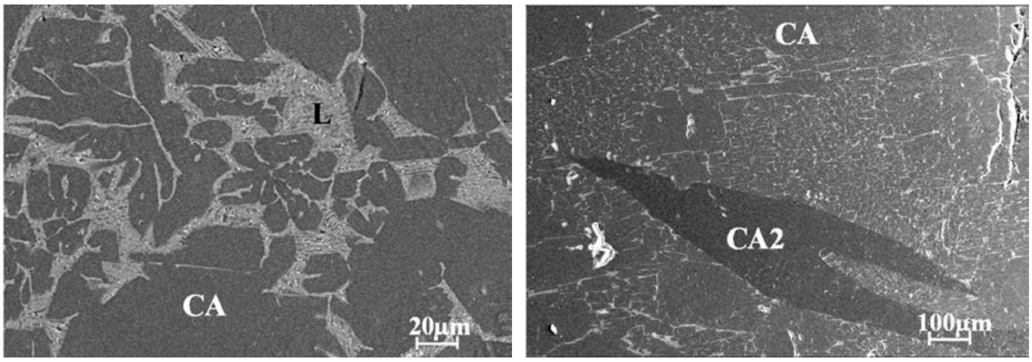
Fig. 1 and Fig. 2 are the back-scattered scanning electron microscope (SEM) micrographs for the quenched slag samples involving the liquid with the equilibrated solid phase(s) respectively at 1450°C and 1550°C obtained in this work. For $CaO-Al_2O_3-FeO_x$ system either at 1450°C or at 1550°C, the results contain two different cases, i.e. the two-phase coexistence and the three-phase coexistence. At 1450°C, the two phases contain liquid (L) in equilibrium with $CaAl_4O_7$(CA2) or $CaAl_2O_4$(CA), while at 1550°C, the two phases are liquid (L) and $CaAl_2O_4$(CA). On the other hand, the three-phase coexistence contains liquid (L), $CaAl_2O_4$(CA) and $CaAl_4O_7$(CA2) at either 1450°C or 1550°C. For $SiO_2-Al_2O_3-FeO_x$ system at 1450°C, the results contain two different cases, two phases, liquid (L) and Mullite(M) equilibrated coexistence, and three phases, liquid (L)+Mullite(M)+SiO_2(S), equilibrated coexistence. While at 1550°C, only two phases, liquid (L) and Mullite(M) have been found from this system of equilibrated coexistence.



(a) Liquid(L), $CaO \cdot 2Al_2O_3$ (CA2) at 1450°C

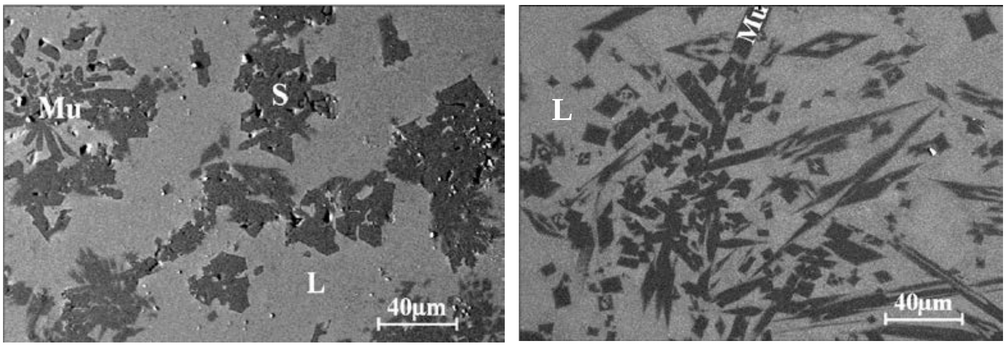


(b) Liquid(L), $CaO \cdot Al_2O_3$ (CA), $CaO \cdot 2Al_2O_3$ (CA2) at 1450°C



(c) Liquid(L), CaO·Al_2O_3 (CA) at 1550°C (d) Liquid(L), CaO·Al_2O_3 (CA), CaO·$2Al_2O_3$ (CA2) at 1550°C

Fig.1 Backscattered SEM micrographs of equilibrated CaO-Al_2O_3-FeO_x slag samples.



(a) Liquid(L), Mullite (Mu), SiO_2(S) at 1450°C (b) Liquid(L) and Mullite (Mu) at 1550°C

Fig.2 Backscattered SEM micrographs of equilibrated SiO_2-Al_2O_3-FeO_x slag samples.

3.2 Liquidus for the CaO-Al_2O_3-FeO_x and SiO_2-Al_2O_3-FeO_x systems

Fig. 3 shows the comparision between the experimental and the calculated liquidus for CaO-Al_2O_3-FeO_x system at 1450°C and 1550°C with the oxygen partial pressure of 10^{-4} atm. The experimental results in the present work are in good agreement with the calculated liquidus by FactSage 6.1. The liquid area mainly locates within these regions where the Al_2O_3 contents are less than 50mass%. With the temperature rising from 1450°C to 1550°C, the liquid area of CaO-Al_2O_3-FeO_x system enlarges and it moves extremely to the high Al_2O_3 region, and the primary phase field of CaO·Al_2O_3 reduces. However, the shape of liquid region at the primary phase field of CaO shows no distinct change with the rising temperature.

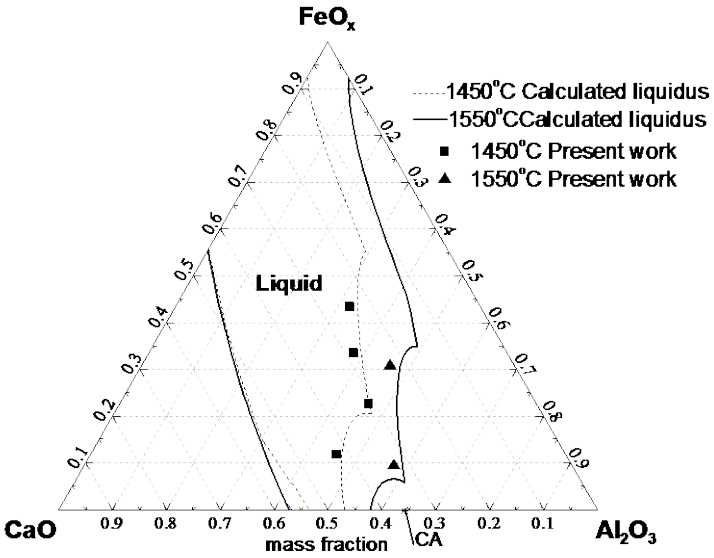


Fig.3 Liquidus of CaO-Al_2O_3-FeO_x system with $P_{O_2}=10^{-4}$ atm

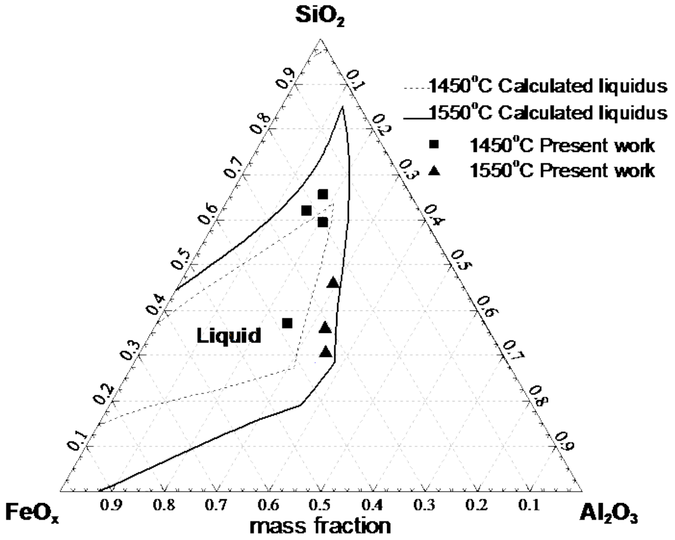


Fig.4 Liquidus of SiO_2-Al_2O_3-FeO_x system with $P_{O_2}=10^{-4}$ atm

The effect of temperature on the liquidus for SiO_2-Al_2O_3-FeO_x system is shown in Fig. 4. At the oxygen partial pressure of 10^{-4} atm, the shapes of liquidus for SiO_2-Al_2O_3-FeO_x system are approximately the same at 1450°C as well as 1550°C. The good agreement can be noted between the present results and the predicted liquidus. With the temperature rise from 1450°C to 1550°C, the liquid phase area enlarges to the high iron oxide region as well as to the primary phase field of mullite. The range of iron oxide content for the liquid area changes from 63~85 mass% to 55~100 mass%.

4. Conclusions

For the intermediate oxygen partial pressure of 10^{-4} atm, the liquidus and phase relations of $CaO-Al_2O_3-FeO_x$ system, $SiO_2-Al_2O_3-FeO_x$ systems at 1450°C and 1550°C were investigated by high temperature equilibrium experiments. The present results were compared with the calculated ones based on FactSage 6.1. The effects of temperature on the equilibrium phase relations and liquidus of $CaO-Al_2O_3-FeO_x$ and $SiO_2-Al_2O_3-FeO_x$ oxide systems are appreciable. For $CaO-Al_2O_3-FeO_x$ system, both two-phase and three-phase coexistence regions are observed at either 1450°C or 1550°C, but the equilibrated phases in the two-phase region are different for the two temperatures. For $SiO_2-Al_2O_3-FeO_x$ system, only two-phase region is found at 1550°C, and the liquid area enlarges to the high iron oxide region as well as to the primary phase field of mullite with rising the temperature. Both the liquid areas of the two systems enlarge with rising the temperature. For $CaO-Al_2O_3-FeO_x$ system, the liquid area enlarges and moves to the Al_2O_3-rich region with temperature rising from 1450°C and 1550°C. While for the $SiO_2-Al_2O_3-FeO_x$ system, the liquid region extends to the high iron oxide region as well as to the primary phase field of mullite.

Acknowledgement

This research work was funded by the National Natural Science Foundation of China (Grant No. 50974034), National Natural Science Foundation of China (Grant No. 51074039), and the Royal Netherlands Academy of Arts and Science (KNAW) (Project 10CDP026).

References

[1] Y. Xiao, M. Oorsprong, Y. Yang and J.H. Voncken. Vitrification of bottom ash from a municipal solid waste incinerator. *Waste Management*, 2008, 28(6), p1020-1026.

[2] S. Y. Kim, T. Matsuto, and N. Tanaka. Evaluation of pre-treatment methods for landfill disposal of residues from municipal solid waste incineration. *Waste Management & Research*, 2003, 21(5), p416-423.

[3] R. R. Dayal, F. P. Glasser. Phase relations in the system $CaO-Al_2O_3-Fe_2O_3$. *Sci. Ceram*, 1967, 3, p191-214.

[4] A. Muan, C. L. Gee. Phase equilibrium studies in the system iron oxide-$A1_2O_3$ in air and at 1 atm O_2 pressure. *Journal of the American Ceramic Society*, 1956, 39(6), p207-214.

[5] E. T. Turkdogan. Physical chemistry of high temperature technology, Academic Press, New York, 1980, p7.