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Phase equilibria in the ZnO-“FeO”-SiO_2-CaO system at Po_2 10^{-8} atm

Hongquan Liu[a], Zhixiang Cui[b], Mao Chen[a,*], Baojun Zhao[a]

[a] *School of Chemical Engineering, The University of Queensland, St Lucia, Queensland 4072, Australia*
[b] *Dongying Fangyuan Nonferrous Metals Co., Ltd, Dongying City, Shangdong 257000, China*

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ABSTRACT

Experimental investigations on the phase equilibria in the ZnO-“FeO”-SiO_2-CaO system have been carried out with 2, 4 and 6 wt pct CaO at 1523, 1543 and 1573 K under Po_2 10^{-8} atm. The experimental techniques involve high-temperature equilibration, quenching and electron probe X-ray microanalysis. The results indicate that when CaO content in the liquid phase increases, the liquidus temperature increases in the spinel primary phase field and decreases in the SiO_2 primary phase field. The partitioning of ZnO shows that ZnO concentration in the liquid phase is higher than that in the spinel phase. The phase equilibrium information can be used to assist the industry processes and also for the development of the thermodynamic database.

1. Introduction

The ZnO-“FeO”-SiO_2-CaO system forms the basis of slag compositions in the non-ferrous metals smelting, such as the copper smelting and converting processes [1] as well as the lead and zinc smelting processes [2]. In the high-temperature processes, in addition to the CaO content from the ores, lime (CaO) is often added to adjust the slag viscosity of the melt [1,3,4], so CaO is commonly present in the slag at a low but not negligible concentration. In the present study, the ZnO-“FeO”-SiO_2-CaO system at the intermediate oxygen partial pressure (Po_2 10^{-8} atm), which is close to the actual industrial copper smelting process, was investigated.

The critical literature review shows that no study on the ZnO-“FeO”-SiO_2-CaO system at Po_2 10^{-8} atm has been experimentally investigated. Dobrotsvetov et al. [5] investigated the system along the join $CaFeSiO_4$–Zn_2SiO_4 by applying DTA, microscopy, chemical analysis and XRD. Another study on the system was performed by Lenz and Lee [6] under the stream of 90% N_2, 5.2% CO_2 and 4.8% CO using DTA technique, and the liquidus temperatures were measured without examining the phases and their compositions after the experiments. Jak et al. [2,7] conducted the phase equilibrium studies in ZnO-“FeO”-(SiO_2 + CaO) system with varied CaO/SiO_2 ratios under the metallic iron saturation condition by applying the “pie-type” sample method [8]. The experimental studies on the CaO-ZnO-SiO_2 sub-system were conducted by Segnit [9] with temperatures ranging from 1433 to 1863 K in platinum crucibles, and the quenched samples were examined by the petrographic microscope. Assessments on the Ca-Fe-O-Si system was performed by Selleby [10] in air, CO_2 atmosphere and iron saturation condition respectively.

The Phase equilibrium studies in the ZnO-“FeO”-SiO_2 system, ZnO-“FeO”-SiO_2-Al_2O_3 system and ZnO-“FeO”-SiO_2-MgO system at Po_2 10^{-8} atm [11–13] have shown that big differences exist between the systems at Po_2 10^{-8} atm and the systems under iron saturation conditions [2,7], while the FactSage 7.0 predictions [14] do not agree with the measurements in all three systems [11–13]. In the present study, the phase diagrams of ZnO-“FeO”-SiO_2-CaO system at Po_2 10^{-8} atm with 2, 4, 6 wt% CaO were constructed experimentally.

2. Experimental

The detailed experimental procedures used in the present study involve high-temperature equilibration, quenching and EPMA [11–13]. The oxygen partial pressure of the slag was controlled by the CO-CO_2 gas mixture, and the reaction rates between the liquid slag and the gas are relatively slower comparing to the reactions between liquid slag and primary solid phase. However, a certain amount of zinc oxide in the slag could be reduced at different temperatures resulting in lower ZnO in the slag. In order to attain the equilibration rapidly and reduce the vaporization of zinc oxide, master slags were prepared in the conditions of the target temperature and oxygen partial pressure. In the experiments, two master slags, zinc silicate master slag and iron silicate master slag as shown in Table 1, were firstly prepared by SiO_2 (99.9 pct, Alfa Aesar) with ZnO (99.9 pct, Sigma-Aldrich) and ‘FeO’ respectively. ‘FeO’ was prepared from iron foil (99.5 + pct, Goodfellow Cambridge Ltd) under 10^{-8} atm at the same temperature required for the final equilibration. CaO was obtained by heating the calcium carbonate

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[*] Corresponding author.
E-mail address: mao.chen@uq.edu.au (M. Chen).

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Table 1
Master slags used in the study.

Master slag	Temperature	Po_2 (atm)	Composition (wt pct)		
			ZnO	SiO_2	"FeO"
Zinc silicate	1773 K (1500 °C)	0.21	74.4	25.6	0.0
Iron silicate	Same as final equilibration temperature	10^{-8}	0.0	33.0	67.0

(99.0 + pct, Sigma-Aldrich) at 1173 K overnight, and then mixed with the iron-silicate master slag and zinc-silicate master slag using agate mortar and pestle. It should be noted that excess ZnO was added in the starting mixture to compensate the possible loss of ZnO during the equilibration. After pelletizing, the mixture (around 0.15 g) was placed on a suitable substrate. In the present studies, SiO_2 substrates were used for the experiments in the SiO_2 primary phase field, and platinum wire baskets (99.9 pct, Cookson Ltd) were used in the spinel, olivine and willemite primary phase fields.

The equilibrium experiments were carried out in a vertical reaction tube furnace [11–13]. A working thermocouple protected by a re-crystallized alumina sheath was placed inside the reaction tube to monitor the actual temperature of the sample. The working thermocouple was periodically calibrated against the standard thermocouple (supplied by the National Measurement Institute of Australia, NSW, Australia). The overall absolute temperature uncertainty was estimated to be ± 3 K. Mixtures of CO-CO_2 gases at different CO/CO_2 ratios were used to obtain the oxygen partial pressure 10^{-8} atm at different temperatures. The oxygen partial pressures at different temperatures were periodically confirmed by the yttria-stabilized zirconia solid electrolyte cell oxygen probe (SIRO$_2$, DS-type oxygen probe; Australian Oxytrol Systems, Victoria, Australia) before starting the equilibrium experiments. The results of the measurements were within the accuracy of the DS-type oxygen probe (close to log PO_2 of ± 0.1 units [PO_2 in atm]).

The mixture was suspended in the hot-zone of reaction tube furnace with the CO_2/CO passing through to maintain Po_2 10^{-8} atm to attain the final equilibration. The necessary equilibrium time for the samples were tested to be between 20 min and 90 min at different temperatures in different primary phase fields at the beginning of the study. The tests demonstrated that the composition of the liquid phase in the samples of different holding time kept the same but the solid proportions varied. It can be explained by the phase rules that the change of bulk composition in the same primary phase field at a constant temperature, which is under the liquidus temperature, will only change the liquid to solid ratio without changing the compositions of the liquid and solid phases. Only the compositions of the liquid and solid phases were used for construction of the phase diagram. Therefore, the change of the bulk composition of the sample during the equilibrations does not change

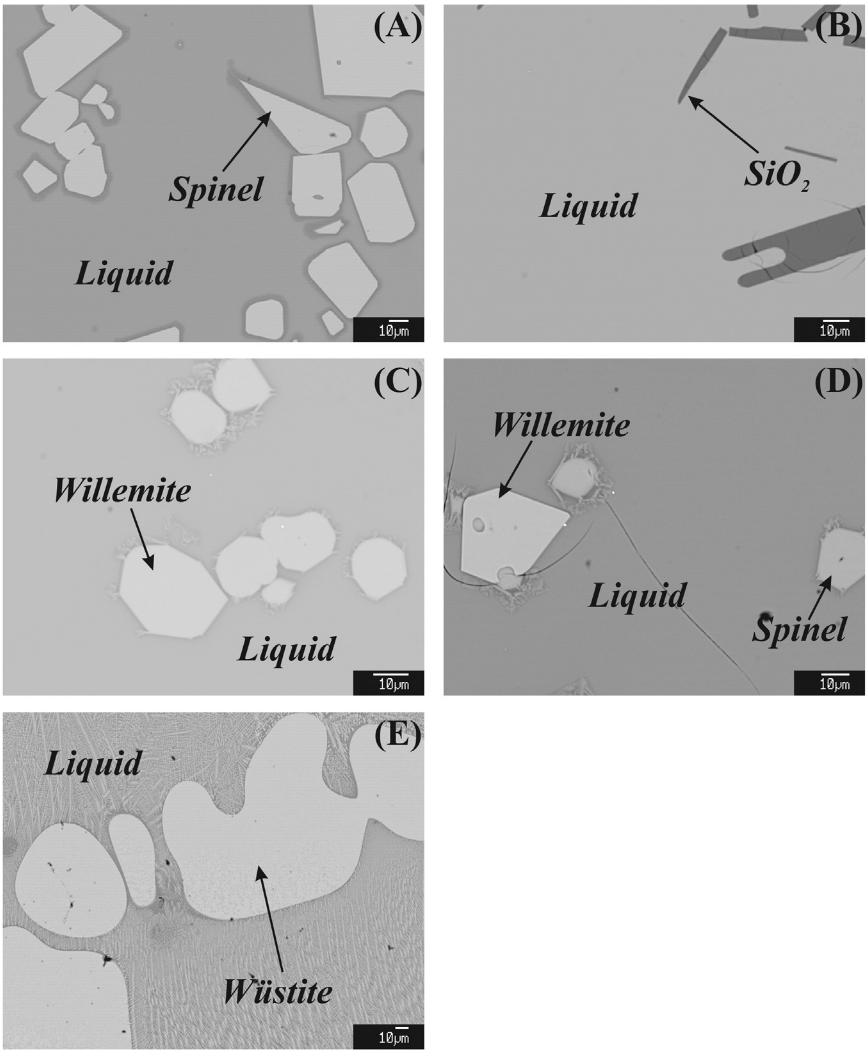

Fig. 1. Microstructures of quenched samples showing liquid in equilibrium with: (A) Spinel; (B) SiO_2; (C) Willemite; (D) Spinel and Willemite and (E) Wüstite at Po_2 10^{-8} atm.