Phase Equilibria Study of the ZnO-“FeO”-SiO_2-Al_2O_3 System at Po_2 10^{-8} atm

HONGQUAN LIU, ZHIXIANG CUI, MAO CHEN, and BAOJUN ZHAO

Phase equilibria studies on ZnO-“FeO”-SiO_2-Al_2O_3 system have been carried out in the temperature range between 1523 K and 1573 K (1250 °C and 1300 °C) at Po_2 10^{-8} atm. Experimental techniques applied in the present study include high temperature equilibration, quenching, and electron probe X-ray microanalysis (EPMA). The compositions of the phases present in the quenched samples were measured by EPMA and used to construct phase diagrams of the pseudo-ternary sections at fixed Al_2O_3 content. The experimental results show that, spinel, SiO_2, and willemite are the major primary phase fields in the composition range investigated. With 2 wt pct Al_2O_3 content in the liquid phase, the liquidus temperature can be increased by 35 K in the spinel primary phase in comparison with Al_2O_3-free system. The partitioning of ZnO and Al_2O_3 between the spinel and liquid phases is also discussed in the paper.

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I. INTRODUCTION

SLAGGING is critically important in the pyrometallurgical processes to produce metals which closely relates to the slag chemistry under the operational conditions.[1,2] In order to optimize the operational parameters, *e.g.*, concentrates, flux compositions, and temperature for pyrometallurgical processes with high efficiency, less energy consumption, and high metal recovery, it is imperative to obtain accurate information of phase equilibria for the slag system.

Zn-Fe-Al-Si-O system forms the basis of the slags in non-ferrous metal pyrometallurgical processes, such as Imperial smelting furnace (ISF), Kivcet, QSL, Ausmelt, and Isamelt processes,[3] as well as oxygen bottom blowing copper smelting process.[4] The oxide components are introduced into the slag phase from the concentrates and fluxes. Meanwhile, zinc-bearing slags are also produced in the secondary metal production and in the zinc-bearing waste recycling processes.[5,6] However, these processes are generally operated at varied temperatures and oxygen partial pressure (Po_2), *e.g.*, the operating temperature is 1423 K (1150 °C) with Po_2 close to 10^{-11} to 10^{-13} atm in lead blast furnace,[7] while operating temperature is around 1453 K (1180 °C) with Po_2 close to 10^{-8} atm in a Fangyuan oxygen bottom blowing copper smelting furnace,[4,8] which both have a profound effect on the phase equilibria behavior and physicochemical properties of the slag.[9]

Previous studies on the ZnO-containing copper smelting slag systems had been carried out under metallic iron saturation,[3,10–19] of which the composition range investigated was relevant to the lead and zinc blast furnace slags. By applying “pie-type” sample of which inner part was ZnO-containing master slag wrapped by metallic iron foil approach, Zhao *et al.*[3,12,15–18] studied ZnO-“FeO”-Al_2O_3-CaO-SiO_2 and higher order systems with varied CaO/SiO_2 and (CaO + SiO_2)/Al_2O_3 ratios under the metallic iron saturation. The results showed that Al_2O_3 content increases the liquidus temperature in the spinel primary phase field. Yamaguchi *et al.*[6] measured the activities of ZnO in the CaO-SiO_2-FeO_x-Al_2O_3 slag with Po_2 fixed at around 10^{-11} atm. They found that the ZnO activities were increased with the addition of Al_2O_3 in the slag, and no phase relations were reported in their study. Our previous work on the ZnO-“FeO”-SiO_2 system at 10^{-8} atm[20] indicated major difference on the phase equilibria behavior under varied Po_2. The results at iron saturation cannot be directly applied to the copper smelting slags due to the significant difference of Po_2 between these processes.

Meanwhile, no phase equilibria work has been reported on the ZnO-“FeO”-SiO_2-Al_2O_3 system at Po_2 10^{-8} atm. With an aim to further improve the understanding of the ZnO-containing copper smelting slag, the phase equilibria studies on the ZnO-“FeO”-SiO_2-Al_2O_3 system with Al_2O_3 concentration up to 6 wt pct have been carried out at Po_2 10^{-8} atm.

II. EXPERIMENTAL

The detailed experimental procedure used in the present study is similar to that reported in the previous work.[4,20] Briefly, two master slags, SiO_2-FeO and ZnO-SiO_2-Al_2O_3 were firstly prepared. The zinc-silicate master slag was prepared by preheating the mixture of

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Table I. Experimentally Determined Phases Compositions in the ZnO-“FeO”-SiO_2-Al_2O_3 System at 1523 K (1250 °C) at Po_2 10^{-8} Atm

			Composition (Wt Pct)			
Experiment No.	Temperature [K (°C)]	Phase	ZnO	SiO_2	“FeO”	Al_2O_3
240	1523 (1250)	liquid	22	37.6	36.5	3.9
		spinel	14.5	0.4	80.5	4.6
241	1523 (1250)	liquid	21.7	37.1	37.3	3.9
		spinel	14	0.3	81.3	4.4
242	1523 (1250)	liquid	22.5	37.5	36.2	3.8
		spinel	14.5	0.4	80.6	4.5
260	1523 (1250)	liquid	20	37.2	39.2	3.6
		spinel	12.9	0.4	82.3	4.4
261	1523 (1250)	liquid	19.5	37.1	39.7	3.7
		spinel	12.6	0.5	83.0	4.0
272	1523 (1250)	liquid	12.6	35.3	50.2	1.9
		spinel	6.8	0.4	91.2	1.6
276	1523 (1250)	liquid	12.9	35.0	50.3	1.8
		spinel	6.7	0.4	91.3	1.5
322	1523 (1250)	liquid	0	24.6	74.1	1.3
		spinel	0.0	0.7	97.5	1.7
323	1523 (1250)	liquid	0	25.5	71.9	2.6
		spinel	0	0.7	95.7	3.6
334	1523 (1250)	liquid	0	26	70.2	3.8
		spinel	0	0.6	93.9	5.5
405	1523 (1250)	liquid	21.5	37.3	36.6	4.6
		spinel	14.3	0.3	80.2	5.2
437	1523 (1250)	liquid	0.0	25.9	72.0	2.0
		spinel	0	0.7	96.4	2.9
438	1523 (1250)	liquid	0	26	72	2
		spinel	0.1	0.5	96.9	2.4
441	1523 (1250)	liquid	0	25.8	72.1	2.1
		spinel	0	0.7	96.4	2.9
443	1523 (1250)	liquid	0.1	31	66.5	2.4
		spinel	0	0.4	97.6	2
457	1523 (1250)	liquid	9.1	38.3	46.5	6.1
		spinel	6.6	0.4	86.9	6.2
458	1523 (1250)	liquid	0.0	27.5	66.7	5.7
		spinel	0	0.5	91.6	7.9
474	1523 (1250)	liquid	9.6	36.1	48.3	6
		spinel	7.3	0.4	84.6	7.7
476	1523 (1250)	liquid	10.1	34.9	48.9	6.1
		spinel	6.8	0.4	85.1	7.7
501	1523 (1250)	liquid	9.0	34.2	52.6	4.3
		spinel	4.5	0.5	90.2	4.9
613	1523 (1250)	liquid	8.1	37.4	51.7	2.8
		spinel	4.6	0.4	92.4	2.5
212	1523 (1250)	liquid	26.2	37.3	33.4	3.1
		SiO_2	0.3	99.3	0.4	0
213	1523 (1250)	liquid	26.2	37.4	33.3	3.1
		SiO_2	0.3	99.4	0.3	0
316	1523 (1250)	liquid	0	37.9	60.3	1.8
		SiO_2	0	98.9	1.1	0
335	1523 (1250)	liquid	0	37.2	61.1	1.7
		SiO_2	0	99.2	0.8	0
336	1523 (1250)	liquid	0.0	38.6	57.9	3.5
		SiO_2	0	99.2	0.8	0
337	1523 (1250)	liquid	0	39.4	55.4	5.2
		SiO_2	0.0	98.5	1.4	0.1
439	1523 (1250)	liquid	0	38.6	57.3	4.1
		SiO_2	0.1	99	0.9	0
440	1523 (1250)	liquid	0	33.5	62	4.5
468	1523 (1250)	liquid	13.0	36.8	45.7	4.4
		SiO_2	0.3	98.8	0.9	0

Table I. continued

Experiment No.	Temperature [K (°C)]	Phase	Composition (Wt Pct)			
			ZnO	SiO_2	“FeO”	Al_2O_3
469	1523 (1250)	liquid	11.7	38.4	43.4	6.5
		SiO_2	0.3	98.7	1	0
471	1523 (1250)	liquid	15.9	37.3	42.2	4.5
		SiO_2	0.5	98.6	0.9	0
539	1523 (1250)	liquid	24.3	36.5	37.2	2
		SiO_2	0.5	98.8	0.7	0
588	1523 (1250)	liquid	13.2	38.7	40.5	7.5
		SiO_2	0.5	98.0	1.3	0.2
642	1523 (1250)	liquid	7.4	36.1	54.3	2.2
		SiO_2	0.2	98.7	1.1	0.0
643	1523 (1250)	liquid	8.0	37.5	50.4	4.2
		SiO_2	0.2	98.8	0.9	0.0
644	1523 (1250)	liquid	7.6	38.5	47.8	6.0
		SiO_2	0.2	98.9	0.8	0.1

ZnO, SiO_2, and Al_2O_3 at 1773 K (1500 °C) in air to obtain homogeneous liquid. The iron-silicate master slag was obtained by pre-equilibration of the mixture of Fe_2O_3 and SiO_2 in the target temperature and Po_2. The final mixture was prepared by mixing the desired proportions of iron-silicate and zinc-silicate master slags with the three components Fe_3O_4, SiO_2, or ZnO. Primary phase substrate technique was applied for the experiments in the primary phase fields of spinel and SiO_2. A platinum basket was used for the experiments in the willemite primary phase field. After pelletising, the mixture (around 0.15 g) was placed in a suitable container and suspended in the hot-zone of the reaction tube with the CO_2/CO mixture passing through to maintain Po_2 at 10^{-8} atm to achieve final equilibration. After equilibration, the sample was quenched into ice water. The obtained sample was then mounted and polished for EPMA.

Optical microscopy was firstly applied to examine the phase assemblages present in the sample. Carbon coating was performed on the QT150TES (Quorum Technologies) prior to electron probe microanalysis (EPMA). A JXA 8200 Electron Probe Microanalyzer equipped with wavelength-dispersive X-ray spectroscopy (Japan Electron Optics Ltd) was applied to microstructures and phase composition analyses. The working voltage and probe current were 15 kV and 15 nA, respectively. The standards used for the analyses were from Charles M. Taylor Co. (Stanford, California): Fe_2O_3 for Fe, Al_2O_3 for Al, and $CaSiO_3$ for Si, and Micro-Analysis Consultant Ltd (Cambridge, UK): ZnO for Zn. The ZAF correction procedure supplied with the EPMA was applied. Although Fe^{2+} and Fe^{3+} are both present in the quenched samples, only metal cation concentrations can be measured by EPMA. Therefore, all the iron was recalculated to “FeO” for presentation purpose only.

III. RESULTS AND DISCUSSIONS

In the present study, phase equilibria in the ZnO-“FeO”-SiO_2-Al_2O_3 system have been determined between 1523 K and 1573 K (1250 °C and 1300 °C) under Po_2 fixed at 10^{-8} atm with Al_2O_3 content up to 6 wt pct. The EPMA results are presented in Tables I, II, and III. The phase diagrams are presented in the form of pseudo-ternary at constant Al_2O_3 concentration as indicated in Figure 1. Three primary phase fields were identified in the composition range studied, including spinel [$(Fe^{2+}, Zn)O{\cdot}(Fe^{3+}, Al)_2O_3$], tridymite ($SiO_2$), and willemite [$(Fe^{2+}, Zn)_2SiO_4$]. The typical microstructures from the quenched samples are presented in Figure 2 that include the equilibrium of liquid with spinel (Figure 2a), tridymite (Figure 2b), willemite (Figure 2c), and with both spinel and willemite (Figure 2d), respectively. The extensive solid solution was measured for spinel and will be further discussed in later sections.

The liquidus surfaces with 2, 4, and 6 wt pct Al_2O_3 on the ZnO-“FeO”-SiO_2-Al_2O_3 system were constructed based on the data listed in Tables I, II, and III, as shown in Figures 3 through 5. In the Figures 3 through 5, the thin solid lines are experimentally determined isotherms, while the thick solid lines represent the experimentally determined boundaries and the thick dash lines indicate the phase boundaries in the areas without experimental data. It can be seen that, the liquidus temperatures mainly decrease in the spinel primary phase field and increase in the tridymite primary phase field with increasing SiO_2 concentration. In the willemite primary phase field, the liquidus temperatures increase with increasing ZnO concentration.

A. *Effects of Al_2O_3 and ZnO on the Primary Phase Fields and Liquidus Temperatures*

Alumina (Al_2O_3), commonly present in the copper smelting slag, is introduced by copper concentrate, silica flux, or fuel. Using the current experimental data, liquidus surfaces at 1523 K (1250 °C) with varied Al_2O_3 contents are constructed as shown in Figure 6. The liquidus temperatures predicted by FactSage[21] are also presented in the figure for comparison. It can be seen from the figure that up to 6 wt pct, Al_2O_3 does not have a significant effect on the size of the fully liquid

Table II. Experimentally Determined Phases Compositions in the ZnO-“FeO”-SiO_2-Al_2O_3 System at 1543 K (1270 °C) Under Po_2 10^{-8} Atm

			Composition (Wt Pct)			
Experiment No.	Temperature [K(°C)]	Phase	ZnO	SiO_2	“FeO”	Al_2O_3
186	1543 (1270)	liquid	28.5	35.5	33	3
		spinel	19.3	0.4	75.9	4.5
187	1543 (1270)	liquid	0.1	22.1	76	1.8
		spinel	0.1	0.6	96.2	3.1
202	1543 (1270)	liquid	0.3	23.6	74.5	1.6
		spinel	0.2	0.6	96.9	2.3
203	1543 (1270)	liquid	2.2	26.9	69.2	1.6
		spinel	1.3	0.6	96.1	2.0
206	1543 (1270)	liquid	20.6	35.5	41.4	2.5
		spinel	11	0.3	86.4	2.3
207	1543 (1270)	liquid	20.2	35.1	42.3	2.5
		spinel	11.3	0.3	85.8	2.6
223	1543 (1270)	liquid	27.8	36.3	33.4	2.5
		spinel	17.6	0.3	79.4	2.7
224	1543 (1270)	liquid	28.0	36.2	33.3	2.5
		spinel	17.7	0.3	79.3	2.7
225	1543 (1270)	liquid	29.5	36.2	31.9	2.4
		spinel	19	0.3	78.1	2.6
226	1543 (1270)	liquid	28.9	36.3	32.3	2.5
		spinel	18.4	0.3	78.5	2.8
250	1543 (1270)	liquid	29.7	35.2	30.9	4.2
		spinel	20.2	0.3	73.2	6.3
252	1543 (1270)	liquid	17.6	35.8	43	3.6
		spinel	11.1	0.4	83.8	4.6
253	1543 (1270)	liquid	33.9	37.9	21.9	6.3
		spinel	27.9	0.3	59.3	12.5
300	1543 (1270)	liquid	0	21.8	76.7	1.5
		spinel	0	0.7	96.7	2.6
305	1543 (1270)	liquid	0	22.7	74.5	2.8
		spinel	0	0.6	94.3	5.1
315	1543 (1270)	liquid	0	23.9	71.8	4.3
		spinel	0	0.6	91.6	7.8
502	1543 (1270)	liquid	10.9	33.3	51.5	4.2
		spinel	6.6	0.4	88.1	4.9
542	1543 (1270)	liquid	0	24.3	69.8	5.9
		spinel	0	0.5	87.6	11.9
582	1543 (1270)	liquid	7.8	33.2	52.8	6.2
		spinel	6.4	0.4	83.9	9.3
584	1543 (1270)	liquid	21.0	36.2	37.3	5.5
		spinel	14.7	0.6	76.2	8.5
585	1543 (1270)	liquid	26.5	36.9	30.8	5.7
		spinel	19.7	0.3	70.9	9.0
598	1543 (1270)	liquid	19.5	35.9	39.1	5.5
		spinel	14.2	0.4	76.4	9.0
612	1543 (1270)	liquid	22.7	34.7	37.3	5.2
		spinel	17.6	0.3	72.8	9.2
747	1543 (1270)	liquid	17.6	34.9	45.2	2.3
		spinel	11.0	0.4	85.5	3.2
211	1543 (1270)	liquid	25.6	38.1	33.3	3
		SiO_2	0.5	98.9	0.6	0
231	1543 (1270)	liquid	29	37.5	31.3	2.2
		SiO_2	0.7	98.7	0.6	0
256	1543 (1270)	liquid	26.4	38.7	30	4.9
		SiO_2	0.6	98.7	0.7	0
321	1543 (1270)	liquid	0	41	52.8	6.2
		SiO_2	0	99.3	0.7	0
451	1543 (1270)	liquid	0	38.9	57	4.1
		SiO_2	0.0	99.2	0.8	0.0
499	1543 (1270)	liquid	0.0	37.7	60.5	1.9
		SiO_2	0.0	99.3	0.7	0.0

Table II. continued

			Composition (Wt Pct)			
Experiment No.	Temperature [K(°C)]	Phase	ZnO	SiO_2	"FeO"	Al_2O_3
540	1543 (1270)	liquid	23.9	37.1	37	2
		SiO_2	0.5	98.8	0.7	0
572	1543 (1270)	liquid	0.0	37.2	61.0	1.8
		SiO_2	0.0	99.2	0.8	0.0
583	1543 (1270)	liquid	14.2	38.9	39.8	7.2
		SiO_2	0.5	98.7	0.8	0.0
586	1543 (1270)	liquid	12.9	37.5	46.8	2.8
		SiO_2	0.4	98.5	1.1	0.0
646	1543 (1270)	liquid	6.8	38.7	50.4	4.1
		SiO_2	0.2	99.1	0.7	0.0
647	1543 (1270)	liquid	0.0	39.3	57.0	3.7
		SiO_2	0.0	99.2	0.8	0.0
648	1543 (1270)	liquid	6.3	39.1	48.7	5.9
		SiO_2	0.1	99.2	0.7	0.0
673	1543 (1270)	liquid	10.4	38.6	45.2	5.9
		SiO_2	0.2	99.0	0.8	0.0
680	1543 (1270)	liquid	9.3	35.9	52.7	2.1
		SiO_2	0.2	99.0	0.8	0.0
205	1543 (1270)	liquid	34.7	35.9	24.8	4.7
		spinel	27.3	0.3	58.8	13.5
		willemite	62.3	28.1	9.4	0.2
289	1543 (1270)	liquid	0	31.6	66.3	2.1
294	1543 (1270)	liquid	0	31.9	66	2.1
297	1543 (1270)	liquid	0	33.4	62.4	4.2
446	1543 (1270)	liquid	0.0	38.5	57.2	4.2
298	1543 (1270)	liquid	35.2	38.0	23.0	3.9
		willemite	63.3	28.8	7.8	0.1
304	1543 (1270)	liquid	34.8	36	24.5	4.7
		willemite	61.8	28.9	9.1	0.2
307	1543 (1270)	liquid	33.6	35.7	26.7	4.0
		willemite	61.8	28.7	9.3	0.2
309	1543 (1270)	liquid	35.2	36.6	22.3	6.0
		willemite	63.5	28.4	7.9	0.2
481	1543 (1270)	liquid	32.8	37.2	28.7	1.3
		willemite	60.6	28.9	10.5	0
482	1543 (1270)	Liquid	33.8	37.5	25.2	3.5
		Willemite	61.8	29.1	9.0	0.0
486	1543 (1270)	Liquid	32.2	36.4	29.8	1.6
		Willemite	61.3	28.3	10.4	0
500	1543 (1270)	liquid	34.5	35.2	25.5	4.8
		willemite	62.2	28.5	9.1	0.2

area surrounded by the isotherms in the spinel and tridymite primary phase fields. Both isotherms move towards high SiO_2 direction. The fully liquid area at 1523 K (1250 °C) determined from the present study is much smaller than that from FactSage prediction[21] at Po_2 10^{-8} atm.

For the industrial implication purposes, the effect of ZnO on the liquidus temperatures in the spinel primary phase field is presented in pseudo-binary sections with Fe/SiO_2 (mass ratio) relevant to the copper smelting slags.[4] It can be seen from Figure 7 that, liquidus temperatures in spinel phase field continuously increased with increasing ZnO concentration regardless of Al_2O_3 concentration. However, it can be seen that the spinel liquidus is more sensitive to ZnO concentration if Al_2O_3 is present. In Al_2O_3-free slag the liquidus temperature is increased by approximately 45 K with 10 wt pct ZnO addition. When 6 wt pct Al_2O_3 is present, the liquidus temperature will be increased by approximately 70 K with 10 wt pct ZnO addition. It also can be seen that, FactSage predictions[21] of the spinel liquidus are much lower than the experimental results. For example, at 2 wt pct Al_2O_3 and 10 wt pct ZnO, the liquidus temperature predicted by FactSage is 70 K lower than that determined in the present study.

Figure 8 shows the effect of Al_2O_3 on the liquidus temperatures in the spinel primary phase field at Fe/SiO_2 weight ratio of 1.5 in the liquid phase. It can be seen that liquidus temperatures in the spinel primary phase field increase with increasing Al_2O_3 concentration at fixed ZnO concentrations. Addition of 6 wt pct Al_2O_3 in the slag can increase the liquidus temperature by 20 K and 50 K depending on the ZnO concentrations in the liquid.

Table III. Experimentally Determined Phases Compositions in the ZnO-“FeO”-SiO_2-Al_2O_3 System at 1573 K (1300 °C) Under Po_2 10^{-8} Atm

			Composition (Wt Pct)			
Experiment No.	Temperature [K (°C)]	Phase	ZnO	SiO_2	“FeO”	Al_2O_3
310	1573 (1300)	liquid	4.7	28.0	65.0	2.3
		spinel	2.8	0.4	93.8	3.0
311	1573 (1300)	liquid	22.8	32.3	40.5	4.4
		spinel	14.6	0.3	76.7	8.4
312	1573 (1300)	liquid	5.9	26.4	65.9	1.8
		spinel	3.1	0.4	94.0	2.6
313	1573 (1300)	liquid	0.9	23.5	74.0	1.6
		spinel	0.4	0.4	97.6	1.6
314	1573 (1300)	liquid	25.6	34.7	34.4	5.2
		spinel	21.4	0.4	69.3	8.9
317	1573 (1300)	liquid	6.4	26.5	65.7	1.4
		spinel	3.3	0.4	94.6	1.7
453	1573 (1300)	liquid	15.2	30.2	50.5	4.1
		spinel	10.5	0.3	80.0	9.2
454	1573 (1300)	liquid	14.3	31.1	48.7	5.9
		spinel	12.4	0.3	73.1	14.2
456	1573 (1300)	liquid	24.0	29.6	44.3	2.1
		spinel	14.2	0.4	81.2	4.2
463	1573 (1300)	liquid	0.0	15.9	81.1	3.0
		spinel	0.1	0.4	92.4	7.1
472	1573 (1300)	liquid	0.0	20.3	73.5	6.2
		spinel	0.0	0.4	83.0	16.6
474	1573 (1300)	liquid	0.0	15.7	81.9	2.4
		spinel	0.1	0.5	93.8	5.7
479	1573 (1300)	liquid	0.0	17.7	78.1	4.1
		spinel	0.0	0.4	89.0	10.6
749	1573 (1300)	liquid	8.3	28.6	60.7	2.4
		spinel	4.9	0.4	90.9	3.7
750	1573 (1300)	liquid	36.6	29.5	31.9	2.1
		spinel	21.8	0.5	74.3	3.5
792	1573 (1300)	liquid	26.1	31.5	40.1	2.2
		spinel	16.4	0.4	78.9	4.3
296	1573 (1300)	liquid	38.1	36.2	21.0	4.7
318	1573 (1300)	liquid	39.9	36.2	19.0	4.9
		willemite	65.3	28.1	6.5	0.2
319	1573 (1300)	liquid	39.5	36.0	19.4	5.2
		willemite	64.7	28.3	6.8	0.2
324	1573 (1300)	liquid	38.2	37.9	20.3	3.6
		willemite	64.6	28.3	7.0	0.1
325	1573 (1300)	liquid	39.4	36.4	20.4	3.8
		willemite	64.1	28.3	7.5	0.1
328	1573 (1300)	liquid	38.9	34.3	22.6	4.3
		willemite	63.7	28.3	7.8	0.2
329	1573 (1300)	liquid	39.6	33.4	23.4	3.6
		willemite	63.6	28.2	8.0	0.2
330	1573 (1300)	liquid	38.6	32.9	25.1	3.4
		willemite	63.5	28.0	8.4	0.2
332	1573 (1300)	liquid	40.1	34.1	20.5	5.3
		willemite	65.3	27.9	6.7	0.2
333	1573 (1300)	liquid	40.2	35.4	19.4	5.0
		willemite	64.8	28.5	6.6	0.2
331	1573 (1300)	liquid	38.4	33.0	25.3	3.3
		willemite	63.3	27.9	8.5	0.2
483	1573 (1300)	liquid	36.3	34.7	28.1	0.8
		willemite	61.7	29.0	9.3	0.0
484	1573 (1300)	liquid	38.5	36.2	20.7	4.6
		willemite	63.8	28.7	7.3	0.2
487	1573 (1300)	liquid	38.5	32.8	24.5	4.2
		willemite	63.4	28.2	8.3	0.1

Table III. continued

			Composition (Wt Pct)			
Experiment No.	Temperature [K (°C)]	Phase	ZnO	SiO_2	"FeO"	Al_2O_3
541	1573 (1300)	liquid	40.5	35.2	17.5	6.8
		willemite	65.5	28.1	6.2	0.2
751	1573 (1300)	liquid	38.0	33.1	26.9	1.9
		willemite	63.0	27.6	9.3	0.1
793	1573 (1300)	liquid	38.0	33.6	25.9	2.6
		willemite	63.0	28.7	8.3	0.0
362	1573 (1300)	liquid	0.0	18.9	78.5	2.6
363	1573 (1300)	liquid	0.0	18.1	77.7	4.2
448		liquid	19.0	31.9	46.8	2.3
503		liquid	3.7	31.6	61.7	3.0
326	1573 (1300)	liquid	36.4	39.6	19.6	4.4
		SiO_2	1.0	98.6	0.4	0.0
327	1573 (1300)	liquid	38.0	39.1	18.6	4.3
		SiO_2	0.9	98.8	0.4	0.0
353	1573 (1300)	liquid	0.0	39.5	58.2	2.2
		SiO_2	0.0	99.1	0.9	0.0
357	1573 (1300)	liquid	0.0	41.1	54.8	4.0
		SiO_2	0.0	98.5	1.4	0.0
361	1573 (1300)	liquid	0.0	41.4	52.9	5.6
		SiO_2	0.0	99.1	0.9	0.0
460	1573 (1300)	liquid	17.2	38.2	40.4	4.2
		SiO_2	0.6	98.3	1.1	0.0
461	1573 (1300)	liquid	19.6	40.1	34.3	6.0
		SiO_2	0.7	98.5	0.8	0.0
504	1573 (1300)	liquid	25.0	38.4	34.7	1.9
		SiO_2	0.6	98.8	0.7	0.0
614	1573 (1300)	liquid	8.3	39.0	48.2	4.6
		SiO_2	0.2	99.0	0.8	0.0
649	1573 (1300)	liquid	8.9	37.9	50.5	2.7
		SiO_2	0.2	99.0	0.8	0.0
650	1573 (1300)	liquid	12.5	39.2	43.7	4.6
		SiO_2	0.3	98.8	0.9	0.0
651	1573 (1300)	liquid	9.5	38.8	45.1	6.7
		SiO_2	0.2	99.1	0.7	0.0
670	1573 (1300)	liquid	9.0	37.1	51.7	2.1
		SiO_2	0.2	98.9	0.9	0.0
671	1573 (1300)	liquid	12.8	38.2	44.7	4.2
		SiO_2	0.3	98.7	1.0	0.0
672	1573 (1300)	liquid	9.2	40.1	44.5	6.3
		SiO_2	0.2	99.0	0.8	0.0

Silica is commonly used as a flux in the copper smelting process to control the slag properties. It is convenient for the industry to use the correlation between liquidus temperature and SiO_2 concentration. Figure 9 shows the liquidus temperature in spinel phase field as a function of SiO_2 concentration (Fe/SiO_2 weight ratio) at fixed 5 wt pct ZnO. It can be seen that spinel and SiO_2 are the major primary phases in the composition range investigated (Fe/SiO_2 weight ratio 1.0 to 3.0). In spinel primary phase field, the liquidus temperatures increase with increasing Fe/SiO_2 weight ratio. In contrast, the liquidus temperatures in the SiO_2 primary phase field decrease with increasing Fe/SiO_2 weight ratio. The minimum liquidus temperature (eutectic between the primary phase fields of spinel and silica) at a given Al_2O_3 concentration increases with increasing Al_2O_3 and move towards low Fe/SiO_2 weight ratio. Clearly it can be seen from the figure that liquidus temperatures predicted by FactSage[21] are much lower than that determined in the present study in both spinel and silica primary phase fields. The above results suggest that it is an effective way to control the operating temperature by tuning the Fe/SiO_2 ratio in the industrial copper smelting operation to offset the effects of Al_2O_3 and ZnO in the slag.

B. *Solid–Liquid Equilibria*

One of the advantages using the present experimental approach is that the compositions of solid phase that in equilibrium with the liquid phase can be measured in the same quenched sample. In the present study, the spinel

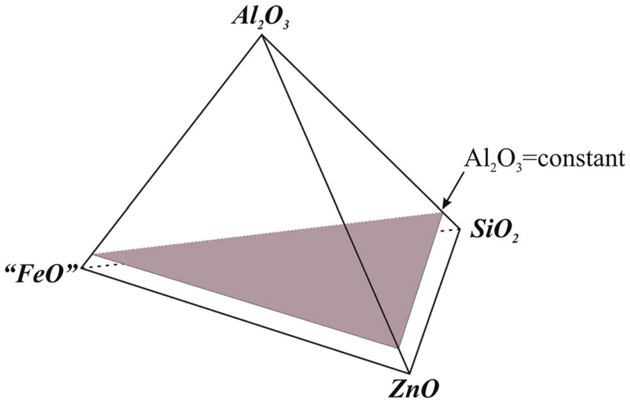

Fig. 1—Pseudo-ternary section in the ZnO-"FeO"-SiO_2-Al_2O_3 system at constant Al_2O_3 content in liquid at Po_2 10^{-8} atm.

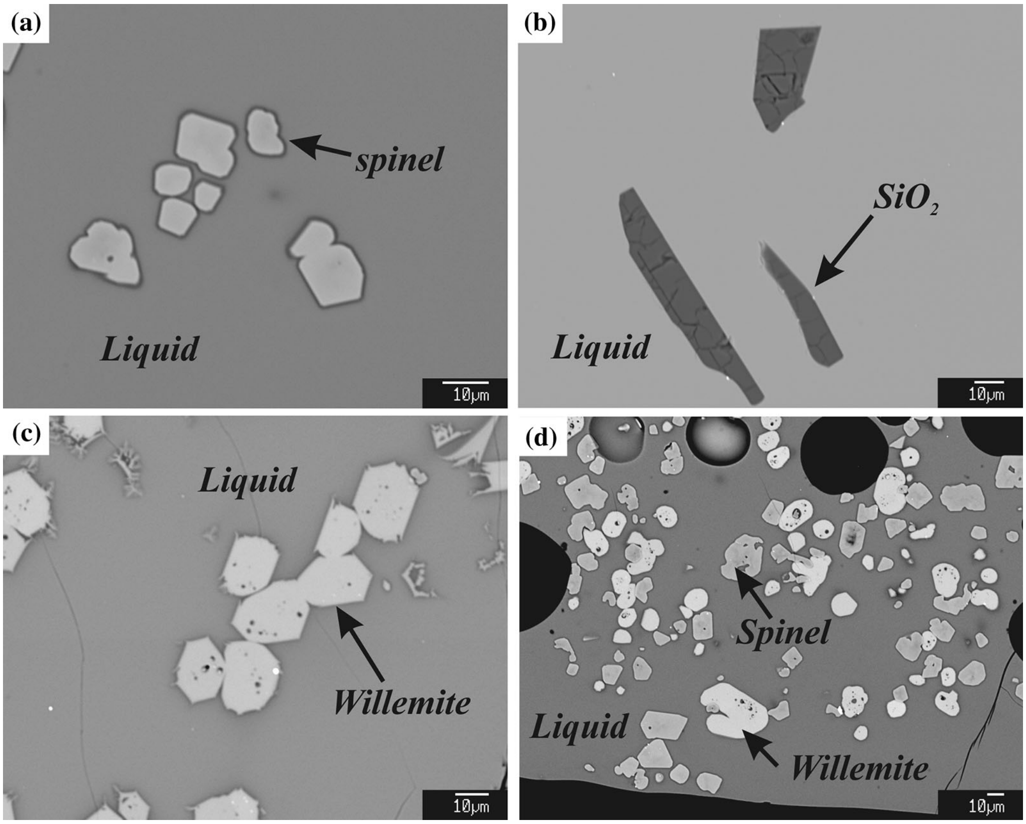

Fig. 2—Typical microstructures of the quenched samples showing equilibrium of liquid with, (*a*) Spinel, (*b*) tridymite, (*c*) Willemite, (*d*) Spinel and Willemite, at Po_2 10^{-8} atm.

phase forms an extensive solid solution [$(Fe^{2+}, Zn)O{\cdot}(Fe^{3+}, Al)_2O_3$] as shown in Tables I, II, and III. In other words, using the current experimental scheme, it is able to provide accurate data on the solid solutions that are very important for the development of thermodynamic modeling.

Copper smelting slag is usually located in the spinel primary phase field which is a solid solution of Fe_3O_4, $ZnFe_2O_4$, $FeAl_2O_4$, and $ZnAl_2O_4$.[18] As an example, the partitioning of ZnO between spinel and liquid is shown in Figure 10. The solid symbols in the figure are the present results and the results from Al_2O_3-free system at Po_2 10^{-8} atm[20] and Al_2O_3-ZnO-"FeO"-SiO_2-CaO at metallic iron saturation[3,15–18] are also shown in the figure for comparison. It appears that Al_2O_3 in liquid can influence the ZnO partitioning and the effect of temperature is not significant. The line passing the symbols represents approximately 5 wt pct Al_2O_3 in the liquid. It can be seen that the ZnO in the spinel is approximately 66 pct of that in the corresponding liquid in the system ZnO-"FeO"-SiO_2-Al_2O_3 at Po_2 10^{-8} atm. This is slightly higher than that in the system

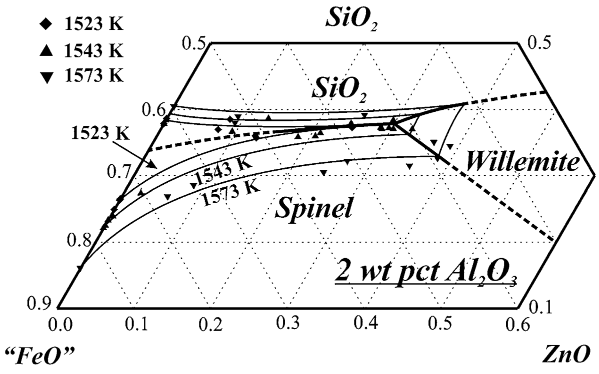

Fig. 3—Experimentally determined pseudo-ternary section ZnO-"FeO"-SiO_2-Al_2O_3 with 2 wt pct Al_2O_3 in the liquid at Po_2 10^{-8} atm.

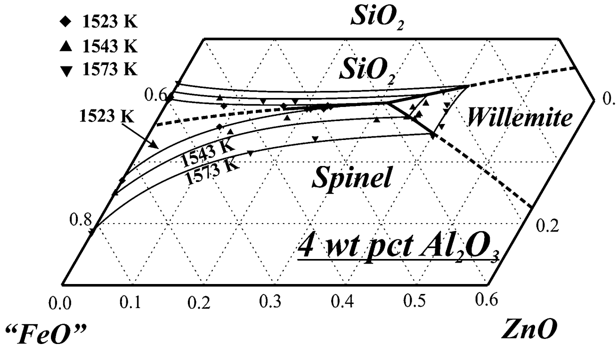

Fig. 4—Experimentally determined pseudo-ternary section ZnO-"FeO"-SiO_2-Al_2O_3 with 4 wt pct Al_2O_3 in the liquid at Po_2 10^{-8} atm.

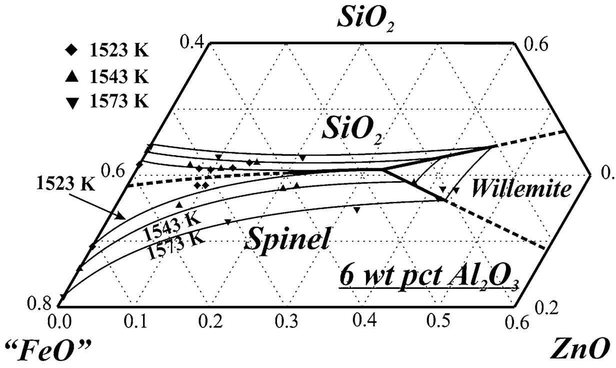

Fig. 5—Experimentally determined pseudo-ternary section ZnO-"FeO"-SiO_2-Al_2O_3 with 6 wt pct Al_2O_3 in the liquid at Po_2 10^{-8} atm.

ZnO-"FeO"-SiO_2 at Po_2 10^{-8} atm,[21] but much lower than that in the system Al_2O_3-ZnO-"FeO"-SiO_2-CaO[3,15–18] at metallic iron saturation. It appears that the ZnO concentration in the spinel is increased with the presence of Al_2O_3 in the slag which suggests that Al_2O_3 can stabilize the ZnO-containing spinel. As shown in Table IV, the Gibbs free energy of formation (ΔG_f) of $ZnAl_2O_4$ is lower than other spinels which indicates the

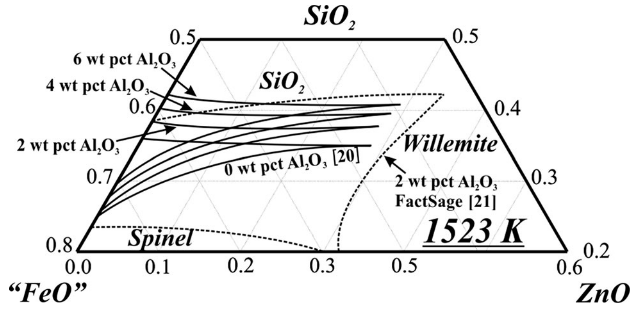

Fig. 6—Liquidus surfaces at 1523 K (1250 °C) with varied Al_2O_3 contents at Po_2 10^{-8} atm.

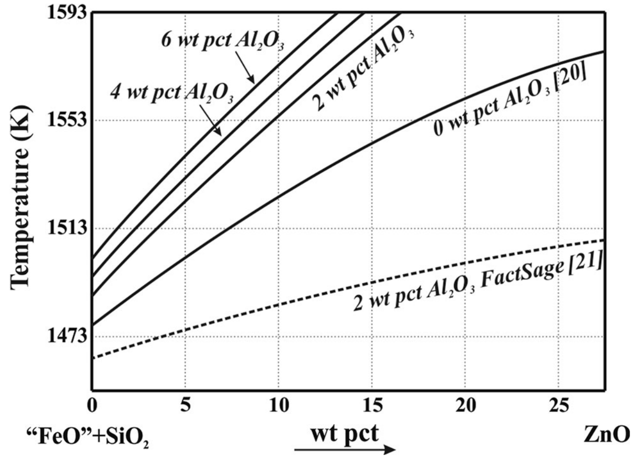

Fig. 7—Comparison of the liquidus temperature between the present study and FactSage predictions[21] in spinel primary phase field as a function of ZnO concentration at fixed Fe/SiO_2 = 1.5 and Po_2 10^{-8} atm.

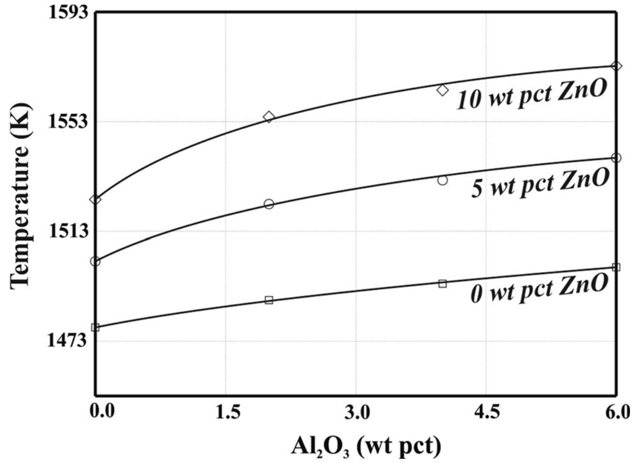

Fig. 8—Liquidus temperature in spinel primary phase field as a function of Al_2O_3 content at fixed Fe/SiO_2 ratio of 1.5 and Po_2 10^{-8} atm.

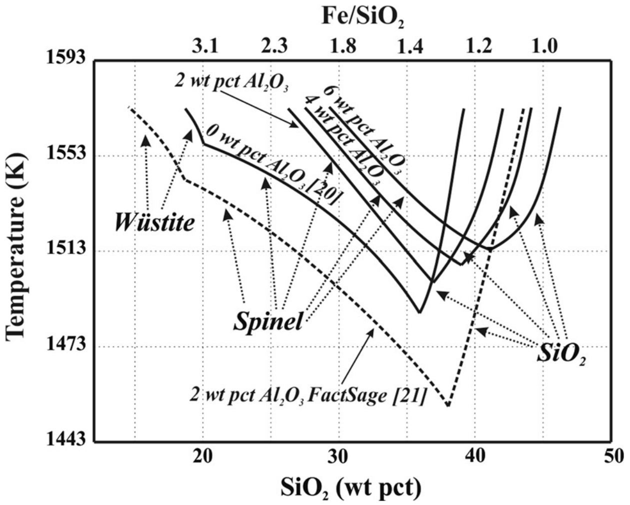

Fig. 9—Liquid temperature as a function of SiO_2 concentration at fixed 5.0 wt pct ZnO and Po_2 10^{-8} atm.

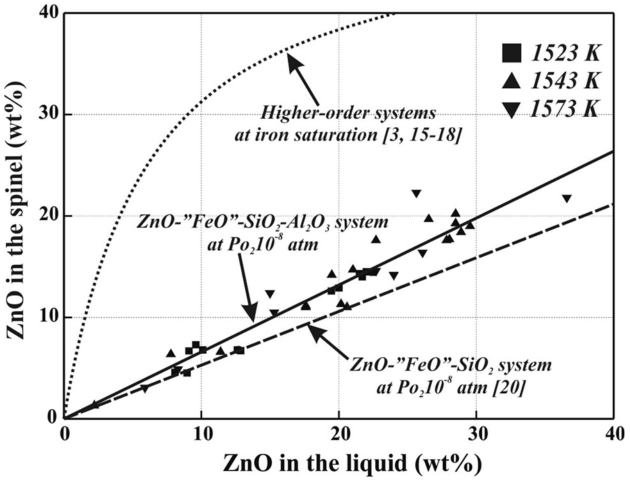

Fig. 10—ZnO partitioning between spinel and liquid at Po_2 10^{-8} atm in comparison with that in equilibrium with metallic iron.[3,15–18]

Table IV. The Gibbs Free Energy of Formation (ΔG_f, kJ mol^{-1}) for Different Types of Spinel at Varied Temperatures[21]

Temperature [K]	Fe_3O_4	$ZnFe_2O_4$	$FeAl_2O_4$	$ZnAl_2O_4$
1523	−1440.1	−1461.9	−2181.2	−2246.8
1543	−1449.6	−1470.6	−2188.9	−2253.8
1573	−1464.0	−1483.8	−2200.6	−2264.5

higher stability of $ZnAl_2O_4$. Moreover, a much higher ZnO content in the spinel can be observed in the Al_2O_3-ZnO-“FeO”-SiO_2-CaO system[3,15–18] at metallic iron saturation as compared to that from higher Po_2. This phenomenon can be explained by the fact that at more reducing condition, *e.g.*, under metallic iron saturation, the Fe_3O_4 and $ZnFe_2O_4$ will be much less stable compared to $ZnAl_2O_4$ and $ZnFe_2O_4$. The results indicate that both Al_2O_3 and Po_2 can affect the ZnO partitioning behavior and the influence of Po_2 is more significant.

C. *Industrial Implications*

The optimization of pyrometallurgical process is largely depending on the improved understanding of the slag properties. Present study has been carried out to fill the knowledge gap of the phase equilibria for the ZnO-containing copper smelting slag. The results in the present study show that the introduction of Al_2O_3 in the slag phase increases the liquidus temperatures in spinel primary phase field resulting in the participation of spinel solid phase. Presence of the spinel phase in the slag has been proven to be beneficial to a longer campaign life of the smelting furnace.[22,23] However, the addition of Al_2O_3 in the slag could lead to a sharp increase of the slag liquidus temperature if ZnO is also present in the slag. Precipitation of the spinel phase may not be easily controlled and it may cause significant operation difficulty.[23] On the other hand, the liquidus temperatures in the spinel primary phase field can be adjusted by Fe/SiO_2 ratio and the proportion of the spinel solid can be managed to be at a proper level.

FactSage[21] is a useful tool for industry to predict the liquidus temperatures and proportion of the solid phase at given temperatures. The present results show that the differences of the liquidus temperatures between FactSage predictions and experimental data are significant. The discrepancies are due to the lack of the accurate data in the ZnO-containing systems under the copper smelting conditions. Experimental results determined in the present study will be used to improve the thermodynamic model to be used for copper industry.

IV. CONCLUSIONS

Phase relations and liquidus temperatures in the ZnO-“FeO”-SiO_2-Al_2O_3 system have been determined at Po_2 10^{-8} atm relevant to copper smelting slags. The results show that, spinel, SiO_2, and willemite are the major primary phase fields in the composition range investigated. The liquidus temperatures increase with the increasing of Al_2O_3 concentration in the liquid phase, accompanying with an extension of the spinel primary phase field. A detailed analysis on partitioning of ZnO between liquid and the conjugated spinel phase shows that ZnO in the spinel is lower than that in the liquid phase. Present study fills the gap of phase equilibria in zinc-containing system at conditions relevant to the copper smelting process. The results will be applied to guide the industrial operation and optimize the thermodynamic database for the zinc-containing system.

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