

Phase Equilibrium Study of ZnO-“FeO”-SiO₂ System at Fixed Po₂ 10⁻⁸ atm

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Keywords: phase equilibrium, copper smelting slag, ZnO-“FeO”-SiO₂

Abstract

Analysis of quenched copper smelting slag from the bottom blown furnace at Dongying Fangyuan Nonferrous Metals Co., Ltd. (Fangyuan) shows that significant ZnO is present in both liquid and spinel phases. Phase equilibria have been investigated in the system ZnO-Fe₂O₃-SiO₂ in air and system ZnO-“FeO”-SiO₂ in equilibrium with metallic iron. These conditions cannot represent copper smelting process in which oxygen partial pressure is around 10⁻⁸ atm. In the present study phase equilibria in the system ZnO-“FeO”-SiO₂ have been carried out at Po₂ 10⁻⁸ atm. A series of experimental difficulties have been overcome to enable the ZnO-containing system to be investigated under reducing conditions controlled by CO-CO₂ gas mixture. The experimental approach includes master slag preparation, high-temperature equilibration, quench and electron probe X-ray microanalysis (EPMA). Phase compositions in the quenched samples were measured by EPMA and used for construction of phase diagram. It was found that the isotherms of the system ZnO-“FeO”-SiO₂ at Po₂ 10⁻⁸ atm are significantly different from those in air or in equilibrium with metallic iron. Presence of ZnO in copper smelting slag significantly increases the liquidus temperature in spinel primary phase field. The partitioning of ZnO in liquid and spinel is also reported in this paper.

1. INTRODUCTION

Copper is the third major industrial metal in the world. About 19 million tons of copper was produced in 2011, while 80% of the total production was obtained by pyrometallurgy where huge amount of energy, both electricity and fossil fuel are consumed.¹⁾ The first commercial bottom blown oxygen smelting furnace (BBF) at Fangyuan has gained great attention due to its excellent performances with high adaptable to raw materials, high copper recovery rate (98%) and energy efficiency.²⁾ However, as a new copper smelting technology, the knowledge of thermodynamics and physico-chemistry in this smelting process is limited, and current research is part of the research program outlined to narrow the gap.

It is well known that slag plays a critical role in the high-temperature processing of copper ore, since metal recovery, slag tapping and refractory consumptions are all closely related to the slag composition under the operating conditions.³⁾ Table 1 shows the compositions of bulk slag, liquid, matte and solid present in a quenched BBF slag. It can be seen that, in addition to the major components “FeO” and SiO₂, the concentration of ZnO is also relatively high. Previous works in this system have been focused in air (Po₂ equal to 0.21 atm)⁴⁾ and at metallic iron saturation (Po₂ is estimated to be around 10⁻¹² atm).⁴⁻⁶⁾ No information can be found relevant to the copper smelting condition in which Po₂ is around 10⁻⁸ atm.²⁾ The present study is focused on the phase equilibrium studies of ZnO-“FeO”-SiO₂ system at Po₂ 10⁻⁸ atm.

Table 1: Compositions (wt%) of phases present in Fangyuan copper smelting slag²⁾

Phases	“FeO”	Cu ₂ O	CaO	SiO ₂	Al ₂ O ₃	As ₂ O ₃	MgO	S	PbO	ZnO	MoO ₃
bulk-XRF	62.2	3.2	1	24.2	3.1	0.1	0.6	1.7	0.5	3.1	0.2
glass	58.4	0.8	1.2	30.5	3.2	0.1	0.7	1.1	0.5	3.3	0.2
spinel	93.7	0.1	0	0.6	3.4	0	0.3	0	0.1	1.7	0.1
matte	10.1	68.9	0	0	0	0.1	0	20.3	0.1	0.2	0.3

2. EXPERIMENTAL METHODOLOGY

Experimental procedure applied in present study is similar to that described in previous papers.^{7,8)} Briefly, the sample was directly quenched into ice water after equilibration at target oxygen partial pressure and temperature, followed by EPMA to determine the compositions of the phases present in the quenched sample.

Under reducing condition, ZnO is progressively reduced and zinc metal vaporises leaving the condensed phases. Previous attempts⁹⁾ to conduct phase equilibrium studies on ZnO-containing systems at controlled P_{O_2} by gas had been proven to be unsuccessful. The research technique has been developed in present study to reduce the vaporization rate of zinc from the slag during the equilibration. 1) ZnO was introduced into zinc-silicate master slag in air to reduce the activity of ZnO; 2) spinel substrate and iron-silicate master slag were prepared in the same conditions (temperature and P_{O_2}) as the equilibration to shorten the final equilibration time of the zinc-containing slags; 3) equilibration time was adjusted to control the ZnO content in slag.

The quenched samples were sectioned, mounted, polished and carbon-coated using QT150TES (Quorum Technologies) Carbon Coater for EPMA examination. A JXA 8200 Electron Probe Microanalyser with Wavelength Dispersive Detectors was used for microstructure and composition analysis. The analysis was conducted with an accelerating voltage of 15 kV and a probe current of 15 nA. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Fe₂O₃ for Fe, CaSiO₃ for Si and ZnO for Zn. The ZAF correction procedure supplied with the electron probe was applied. The average accuracy of the EPMA measurements is within 1 wt pct. Both Fe²⁺ and Fe³⁺ are present in the samples, however, only the metal cation concentrations can be measured using EPMA. For the presentation purpose only, all iron is calculated as “FeO” throughout this paper.

3. RESULTS AND DISCUSSION

(1) Experimental results in “FeO”-SiO₂ system

With an aim to evaluating the experimental methodology applied in current research, a reinvestigation of the “FeO”-SiO₂ system was carried out at the temperature range between 1200-1300°C. The examination of samples indicates the presence of wustite, spinel and tridymite primary phase fields in the phase diagram. The eutectic point between spinel and tridymite primary phase fields was determined to be 1200°C at 33.3 wt% SiO₂ in the present study.

The present results in the system “FeO”-SiO₂ at P_{O_2} 10⁻⁸ atm are compared with previous studies^{10,11)} and FactSage¹²⁾ calculations as shown in Figure 1. It can be seen from Figure 1 that the present data are in good agreement with the previous data.^{10,11)} Experimentally determined liquidus temperatures in the present and previous studies are higher than those predicted by FactSage 6.2¹²⁾ in wustite and spinel primary phase field.

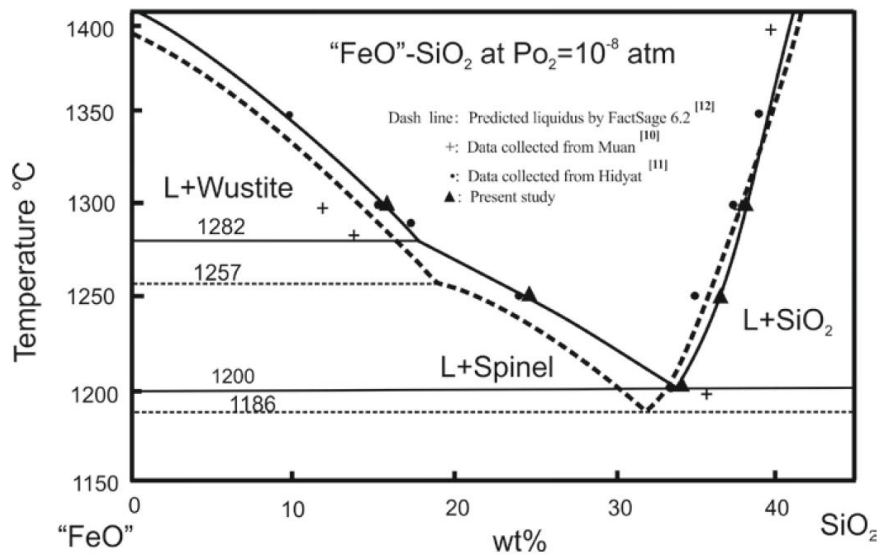


Figure 1: A comparison among current data, previous results^{10,11)} and FactSage 6.2¹²⁾ predictions on “FeO”-SiO₂ system at Po₂ 10⁻⁸ atm

(2) Experimental results in ZnO-“FeO”-SiO₂ system

The liquidus temperatures in ZnO-SiO₂ binary system have been determined in air by different authors.^{13,14)} The eutectic point between tridymite and willemite primary phase fields was reported to be 1448±5 °C at 59 wt% ZnO, and the one between willemite and zincite primary phase fields was reported to be 1502±5 °C at 76.8 wt% ZnO. The previous study in ZnO-“FeO” system was only carried out for sub-solidus under intermediate Po₂ by Hansson et al.¹⁵⁾

The liquidus temperatures in the ZnO-“FeO”-SiO₂ system have been experimentally determined at Po₂ 10⁻⁸ atm between 1200 °C and 1300 °C. The primary phase fields in this system include tridymite, spinel, wustite, willemite and zincite (hypothetically). Both spinel [(Fe²⁺,Zn)O·Fe³⁺₂O₃] and wustite [(Fe²⁺,Zn)O] are iron oxides. Wustite is stable at higher temperatures and spinel is stable at lower temperatures. The typical microstructures of quenched samples in the present study are presented in Figure 2. Figure 2a shows the liquid was in equilibrium with spinel at 1250 °C; Figure 2b shows the liquid was in equilibrium with tridymite at 1250 °C; Figure 2c shows the liquid was in equilibrium with spinel and tridymite at 1200 °C; and in Figure 2d, the liquid was in equilibrium with tridymite and willemite at 1300 °C.

The phase diagram of ZnO-“FeO”-SiO₂ system at Po₂ 10⁻⁸ atm is constructed based on the critically evaluation of the experimental data and understanding of phase rules. It can be seen from Figure 3 that the thick solid line represents experimentally determined boundary between spinel and tridymite, while the thick dash lines are hypothetical boundaries. The thin solid lines are experimentally determined isotherms, while thin dash lines are approximate isotherms. If the slag composition given in Table 1 is normalised to three components ZnO, “FeO” and SiO₂ and plotted in Figure 3, it can be seen that this slag is located in the spinel primary phase field with liquidus temperature of 1250°C. The liquidus temperature of this slag increases with increasing ZnO or “FeO” concentration.

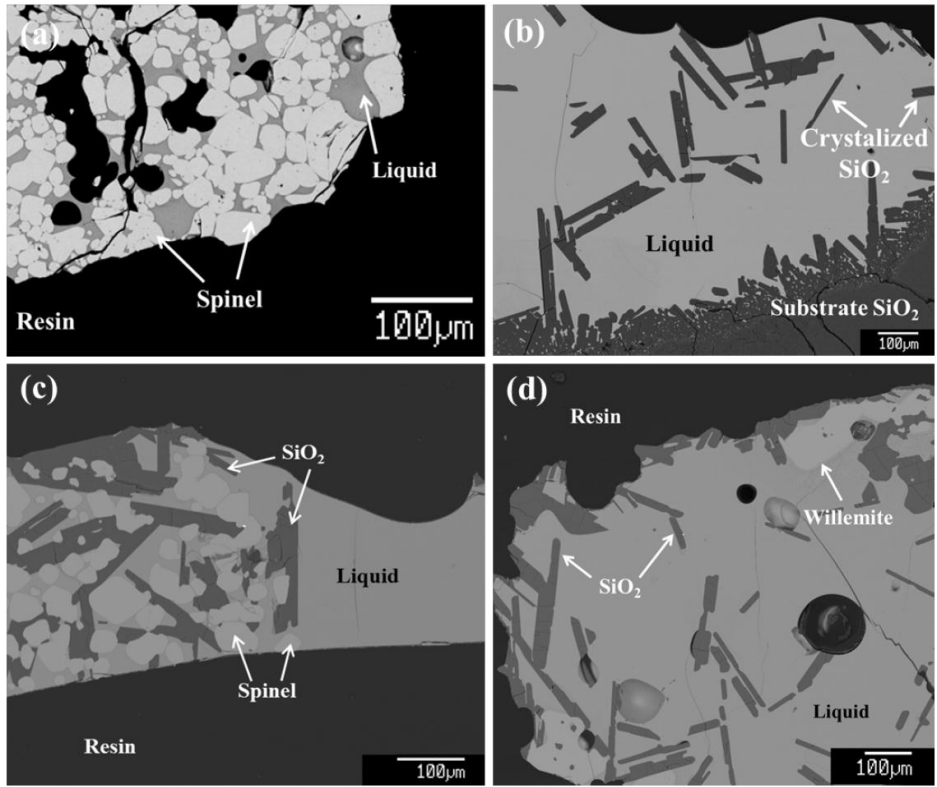


Figure 2: Microstructures of quenched samples showing: (a) liquid equilibrated with spinel; (b) liquid equilibrated with tridymite; (c) liquid equilibrated with spinel and tridymite; (d) liquid equilibrated with tridymite and willemite.

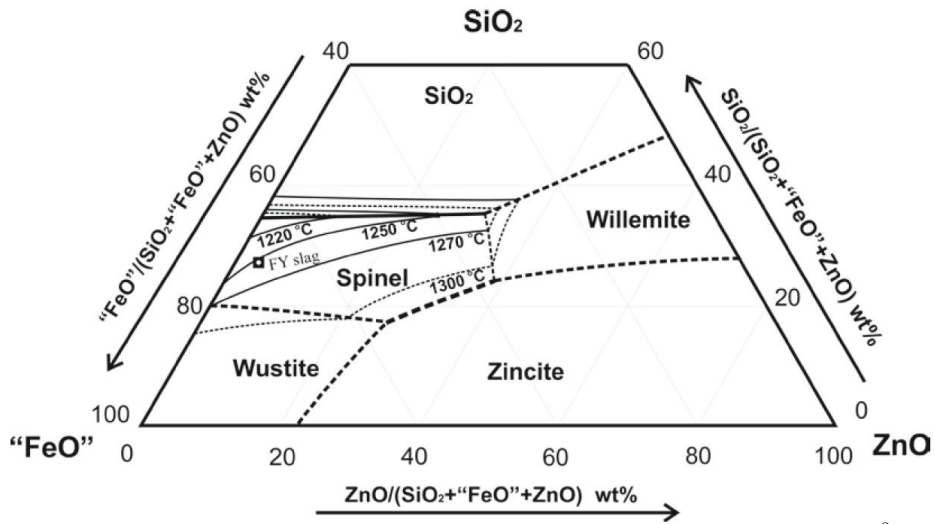


Figure 3: Experimental determined ZnO-“FeO”-SiO₂ phase diagram at Po₂ at 10⁻⁸ atm

A comparison on 1250 °C isotherm between current research and FactSage 6.2¹²⁾ predictions is shown in Figure 4. The solid lines are current results and the dash lines are predicted from FactSage 6.2¹²⁾. It can be seen that FactSage predictions show the liquid is in equilibrium with three primary phases: spinel, willemite and tridymite at 1250 °C. Present study shows that the liquid is only in equilibrium with spinel and tridymite at 1250 °C. The fully liquid area is much smaller in the present study as compared to that predicted by FactSage 6.2¹²⁾.

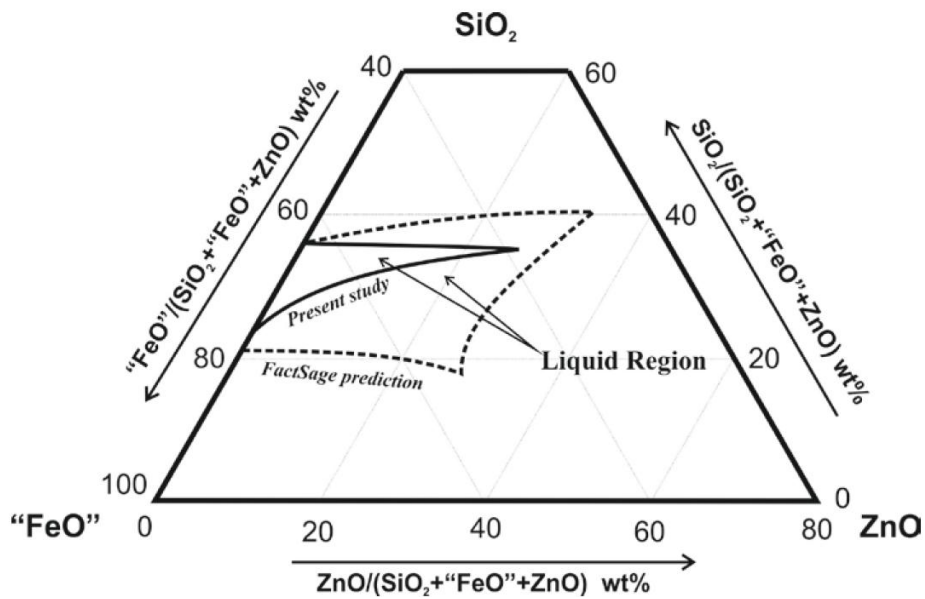


Figure 4: Comparison of 1250 °C isotherm between current study and FactSage 6.2 predictions on ZnO-“FeO”-SiO₂ system under Po₂ at 10⁻⁸ atm

Further comparisons are also carried out in pseudo-binary systems “FeO”-SiO₂ at fixed ZnO (Figure 5) and (“FeO”+SiO₂)-ZnO at fixed Fe/SiO₂ ratio (Figure 6). It can be seen from Figure 5 that, the liquidus temperatures of the slag with 5 wt% ZnO are generally higher than those of ZnO-free slag in the spinel primary phase field. For example, the liquidus temperature of the slag containing 5 wt% ZnO is 1253 °C at 28 wt% SiO₂ (Fe/SiO₂ = 2 in weight), which is 30 °C higher than that of ZnO-free slag. Figure 6 presents the comparison between experimental results and FactSage predictions at fixed Fe/SiO₂ weight ratio of 2. It can be seen that the willemite primary phase field is not present in the experimentally determined phase diagram. The experimentally determined liquidus temperatures are much higher than those predicted by FactSage in the composition range investigated. The enormous difference between current results and FactSage prediction may due to the lack of experimental data at intermediate Po₂ for optimisation of thermodynamical modelling. The data obtained in the present study can be used to improve the thermodynamical modelling.

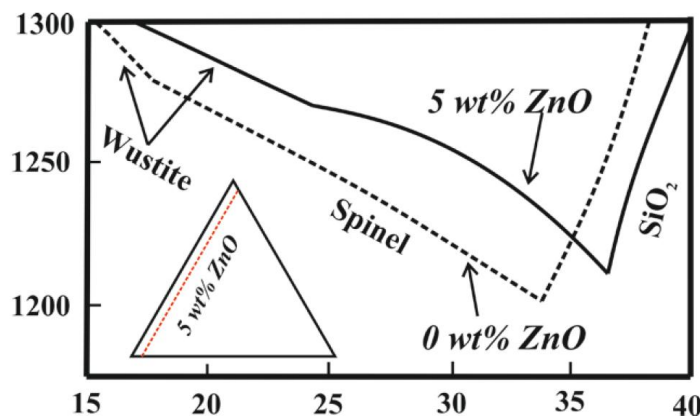


Figure 5: Pseudo-binary “FeO”-SiO₂ at fixed 0 and 5 wt% ZnO at Po₂ at 10⁻⁸ atm

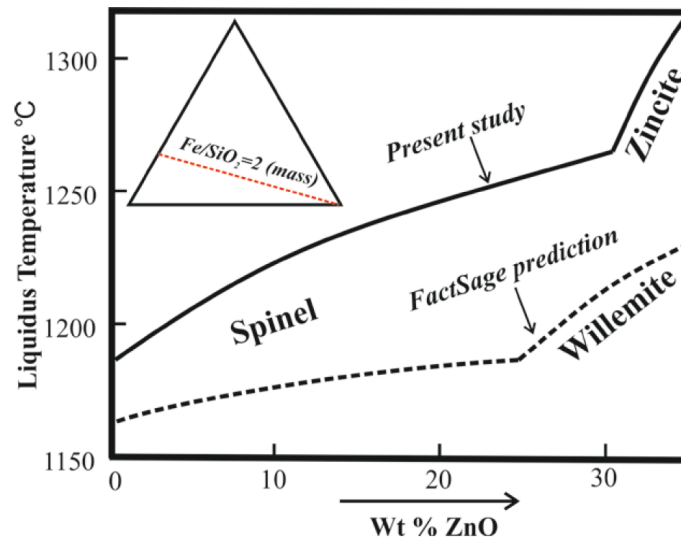


Figure 6: Comparisons between experimental results and FactSage predictions of pseudo-binary ($\text{FeO}+\text{SiO}_2$)-ZnO at fixed $\text{Fe}/\text{SiO}_2=2$ (mass)

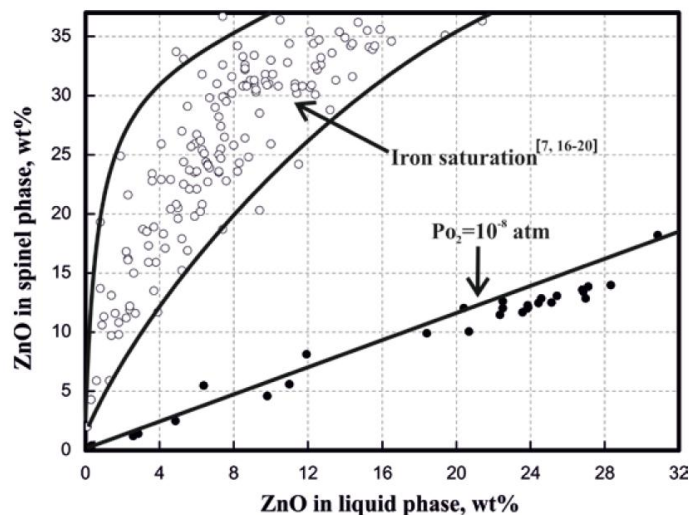


Figure 7: Comparison of partitioning effect of ZnO between liquid phase and spinel phase from current experiments and results under metallic iron saturation^{7,16-20}.

The partitioning of ZnO between spinel and liquid phases has been reported previously in the system ZnO- FeO - Al_2O_3 - CaO - SiO_2 at metallic iron saturation^{7,16-20}. It was found that ZnO in spinel is much higher than that in the corresponding liquid. The comparison is made on the partitioning of ZnO between spinel and liquid at iron saturation and Po_2 10^{-8} atm. It can be seen from Figure 7 that, the solid dots were obtained from current research while the blank dots were extracted from the work under the metallic iron saturation^{7,16-20}. A linear relationship was found between ZnO in spinel phase and liquid phase under Po_2 at 10^{-8} atm as indicated in Figure 7, while the partitioning of ZnO in equilibrium with Fe at different ZnO concentration was found to be limited in some area. Besides, the ZnO solubility in spinel slightly increase with the increase of ZnO concentration in liquid in both conditions, while much lower ZnO goes into spinel phase when Po_2 is 10^{-8} atm compared to that in metallic iron saturation. This difference indicates the reducing condition will help ZnO come into the solid phase, which may be useful information for future ZnO recovery, and will great benefit for the thermodynamic modelling of ZnO-containing systems under Po_2 at 10^{-8} atm. It should be noticed that the difference in Po_2 or compositions in spinel phase ($\text{ZnO}\cdot\text{Al}_2\text{O}_3$, $\text{FeO}\cdot\text{Al}_2\text{O}_3$, $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ may co-exist in metallic saturation) may both lead to this phenomenon. Future work will be carried out to answer question.

4. SUMMARY

Phase equilibrium studies have been conducted under 10^{-8} atm oxygen partial pressure relevant to copper smelting condition with a temperature range from 1200 to 1300 °C. The liquidus temperature and primary phase fields in the “FeO”-SiO₂ and ZnO-“FeO”-SiO₂ systems have been experimentally determined. The liquidus temperatures obtained from current study in spinel primary phase field are higher than the predictions by FactSage 6.2. The liquidus temperatures in spinel primary phase field increase with increasing ZnO concentration in slag. ZnO partitioning between spinel phase and liquid phase has been compared at Po₂ 10^{-8} atm and metallic iron saturation. The result shows that ZnO tends to be more enriched in liquid phase under Po₂ 10^{-8} atm.

ACKNOWLEDGEMENTS

The authors wish to thank

- Dongying Fangyuan Nonferrous Metals Co., Ltd. for providing the financial support to enable this research to be carried out
- The University of Queensland International Tuition Fee Award and China Scholarship Council (CSC) for providing scholarships for Mr. Hongquan Liu
- Mr. Ron Rasch and Ms Ying Yu of the Centre for Microscopy and Microanalysis at the University of Queensland, who provided technical support for the EPMA facilities.

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