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# An experimental study on the phase equilibria of $FeO_x$ -saturated iron silicate slags and metallic copper alloys at 1200–1300 °C



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ARTICLE INFO	A B S T R A C T
Keywords: Copper smelting Magnetite Wüstite Phase diagram Resource efficiency	The equilibrium phase relations between metallic copper alloys and magnetite/wüstite-saturated iron silicate slags were investigated at 1200–1300 °C and $P_{O2}$ of $10^{-10}$ to $10^{-6.5}$ atm. The experiments involved high temperature equilibration of samples in a controlled CO–CO <sub>2</sub> atmosphere, followed by rapid drop quenching and direct measurement of the phase composition using the electron probe microanalysis technique. The equi- librium compositions for the metal and slag phase at different temperatures were displayed as a function of $P_{O2}$ . The present experimental results were compared with data from the literature as well as the thermodynamic assessment using MTDATA thermodynamic software. The present results contribute to the improvement of copper matte and black copper converting and slag cleaning processes.

#### 1. Introduction

The phase equilibria of metallic copper and slag are involved in many pyrometallurgical copper smelting processes, such as copper converting, secondary copper smelting, and slag cleaning processes. Study on the phase equilibria of metallic copper and slag allows to distinguish the distributions of valuable/detrimental elements among different phases and, thus providing guidance for minimizing the loss of valuable metals in slags and removing impurities from metals. A detailed understanding on slag properties equilibrated with metallic copper is essential for the improvement of industrial copper production and for understanding the process chemistry [1].

A lot of work has been so far done for a sulfur-containing Cu–Fe–O–S–Si-(Ca–Al–Mg) system of the copper smelting process. A detailed literature review on these investigations between copper matte and slag can be found in our previous studies [2,3]. Additionally, phase equilibria in the Cu–Fe–O–Si-(Ca–Mg) system have been investigated mainly at silica-saturation. However, only very limited number of studies on the sulfur-free slag-metallic copper equilibria at spine-l/wüstite saturation can be found in literature, due to the difficulties of conducting the experiments with aggressive slag and molten copper in

primary substrate magnetite/wüstite crucibles. In older literature, the phase assemblages were characterized by traditional wet chemical analysis after physically separating matte/metal and slag phases. The physical entrainment of matte/metal droplets in slags as well as an incomplete separation of different phases may have attributed to significant deviations. The significant development of high-temperature isothermal equilibration-quenching-EPMA analysis technique [1] improved the detection accuracy of phase compositions and have been widely used in many recent studies [1,4,5].

Henao et al. [1] investigated phase relations between the "Cu<sub>2</sub>O"-"FeO"-CaO-MgO-Al<sub>2</sub>O<sub>3</sub> slag and metallic copper at  $P_{O2}$  of  $10^{-8.5}$ atm relevant to the slag cleaning process. They constructed the "Cu<sub>2</sub>O"-"FeO"-CaO-MgO-Al<sub>2</sub>O<sub>3</sub> phase diagram, and the spinel (Fe<sub>3</sub>O<sub>4</sub>) and tridymite liquidus for the system were determined. Ilyushechkin et al. [6] investigated phase equilibria of metallic copper and calcium ferrite slags in the Cu-Fe-Ca-O system at 1150-1250 °C. They determined the liquidus for the primary phase fields of spinel (Fe<sub>3</sub>O<sub>4</sub>) and dicalcium ferrite (Ca2Fe2O5) and constructed the isotherms of the "Cu<sub>2</sub>O"-"Fe<sub>2</sub>O<sub>3</sub>"-CaO system at metallic copper saturation. Nikolic et al. obtained for the [7,8] the phase equilibria data "Cu<sub>2</sub>O"-FeO-Fe<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> system at copper saturation under

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#### Table 1

The crucibles used and the calculated gas flow rates at 1200–1300  $^\circ\mathrm{C}$  for target  $P_{\mathrm{O2}}.$ 

Temperature/°C	$Log_{10}P_{O2}/atm$	Gas flow rates/ (mL·min <sup>-1</sup> )		$P_{\rm CO2}/P_{\rm CO}$	Crucible
		CO <sub>2</sub>	СО		
1200	-10	226.3	73.7	3.1	wüstite
	-9	272.0	28.0	9.7	wüstite
	-8	290.5	9.5	30.7	magnetite
1250	$^{-10}$	177.5	122.5	1.5	wüstite
	-9	246.3	53.7	4.6	wüstite
	-8	280.6	19.4	14.5	magnetite
	-7	293.6	6.4	45.8	magnetite
	-6.5	296.4	3.6	81.5	magnetite
1300	-8	263.3	36.7	7.2	wüstite
	-7	287.3	12.7	22.7	magnetite
	-6.5	292.7	7.3	40.3	magnetite

boundary conditions of 1250–1300 °C and fixed oxygen partial pressure of  $10^{-6}$  atm. Liquidus' were obtained for the primary phase fields of spinel and pseudo-wollastonite (CaSiO<sub>3</sub>) at copper saturation. Hidayat et al. [9–11] studied phase relations of the Cu–O–Si–Me systems (Me = Fe, Ca, Al, Mg, and Zn) in equilibrium with metallic copper at 1100–1400 °C. Liquidus and solid composition data were determined in the spinel, willemite and tridymite primary phase fields. In their first paper [9], many points were obtained from a system with one degree of freedom but in inert atmosphere. Moreover, they did an assessment of the Cu–Fe–O–Si system based on the thermodynamic and experimental phase equilibria data [12].

Shishin et al. [13] determined phase relations in the "Cu<sub>2</sub>O"-FeO-Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CaO slags in equilibrium with metallic copper, at 1100–1300 °C and  $P_{O2}$  of  $10^{-12}$  to  $10^{-4}$  atm, using a combined method of experimental work and thermodynamic modeling. The effects of  $P_{O2}$ , temperature, Fe/SiO<sub>2</sub> ratio, and CaO concentration in slag on the slag liquidus and copper loss in the slag were characterized. Sineva et al. [14] equilibrated spinel-saturated FeO<sub>x</sub>-SiO<sub>2</sub> slag and copper alloy at 1250 °C and  $P_{O2}$  of  $10^{-5}$  atm with the presence of Pb, Bi, and Ag in the equilibrium system. However, they mainly focused on the distributions of trace elements between copper alloy and slag. In our previous studies [15–23], the phase equilibria of metallic copper and silica/Al–Fe spinel saturated iron silicate slags in the Cu–Fe–O–Si-(Al–Mg–Ca–K) system were investigated with the presence of varying trace elements.

Based on the aforementioned state-of-the-art technique, only a limited number of studies have been carried out for investigating the metallic copper-slag equilibria in the most basic Cu–Fe–O–Si smelting system at FeO<sub>x</sub> saturation. Therefore, this study was initiated for determining the phase relations between FeO<sub>x</sub>-SiO<sub>2</sub> slags and metallic copper at 1200–1300 °C and at iron oxide saturation over the oxygen partial pressures of  $10^{-10}$ - $10^{-6.5}$  atm.

#### 2. Experimental

The starting materials used for preparing the samples were metallic copper (-625 mesh, 99.9 wt%) and pure oxide powders of Fe<sub>2</sub>O<sub>3</sub> (99.998 wt%) and SiO<sub>2</sub> (-40 mesh, 99.995 wt%), all from Alfa Aesar. The average weight of the samples was approximately 0.4 g, consisting of 0.2 g metallic copper and an equal amount of slag mixture. The metallic copper powder and initial slag mixtures were pelletized to ensure a good contact of components during experiments. The magnetite and wüstite crucibles used for supporting the sample pellets were prepared using iron foil (thickness 0.25 mm, 99.5 wt%), Sigma Aldrich and Merck). The iron foil was folded into a crucible shape and the bottom was formed into a bowl shape using a hemispherical stamping rod. The folded iron foil was subsequently oxidized at 1250 °C and  $P_{O2}$  of  $10^{-7}$  and  $10^{-10}$  atm, respectively. The atmosphere was regulated by a gas



Fig. 1. Schematic of the sample holding technique in the furnace.

mixture of CO (99.99 vol%) and CO<sub>2</sub> (99.999 vol%), all from AGA-Linde (Finland). The target  $PO_2$  and the corresponding gas flowrates of CO and CO<sub>2</sub> at different temperatures were calculated based on the equilibrium constants of reaction (1):

$$2CO(g) + O_2(g) = 2CO_2(g)$$
 (1)

Table 1 shows the gas flow rates calculated by HSC Chemistry software [24] for each target  $P_{O2}$  at 1200–1300 °C, as well as the crucibles used for each experiment. The distributions of trace elements (Ag, Ni, Co and Sn) from the same experiments were reported in our previous publication [25].

High-temperature isothermal equilibration experiments were conducted in a vertical tube furnace (Nabertherm, Lilienthal, Germany, RHTV 120-150/1) heated by MoSi2 heating elements. A calibrated Stype measuring thermocouple (Johnson-Matthey Noble Metals, UK) in a recrystallized alumina sheath was placed next to the sample for monitoring the actual sample temperature. The temperature accuracy was estimated to be within  $\pm 3$  °C. First, the sample was lifted into the cold zone of the furnace and a gas mixture for target  $P_{O2}$  was introduced into the reaction tube for 30 min to stabilize the atmosphere. Then, the sample was raised to the hot zone by a platinum hanging wire and annealed at high temperature. Based on our previous observations, the copper alloy and slag phases can reach equilibrium compositions within 24 h [15-23]. Therefore, all samples were annealed at the experimental temperatures investigated for at least 24 h. Afterwards, the sample was dropped and quenched in an ice-water mixture. Fig. 1 illustrates the schematic of the sample arrangement inside the alumina reaction tube.

The quenched samples were dried, mounted in epoxy (EpoFix, Struers, Denmark), and polished for metallographic examination. The polished sample surfaces were coated with carbon using a carbon evaporator (JEOL IB-29510VET). The microstructures of samples were examined using a Scanning Electron Microscope (SEM; Tescan MIRA 3, Brno, Czech Republic) fitted with an UltraDry Silicon Drift Energy Dispersive X-ray Spectrometer (EDS; Thermo Fisher Scientific, Waltham, MA, USA). The elemental compositions of all phases were determined using a CAMECA SX100 electron probe microanalyzer (EPMA; Cameca SAS, Genevilliers, France) equipped with five wavelength dispersive spectrometers (WDS) at the Geological Survey of Finland (GTK) in

#### Table 2

Standards used and detection limits of EPMA analyzes.

Element	Standard	X-ray	Detection	Detection limits of EPMA/ppmw			
		line	Copper	Slag	Magnetite/ Wüstite		
0	Obsidian	Kα	437	692	606		
Si	Quartz	Kα	155	119	118		
Fe	Hematite	Kα	111	141	158		
Cu	Synthetic metallic copper	$K_{\alpha}$	389	197	199		

Espoo, Finland. An accelerating voltage of 20 kV and a beam current of 60 nA were used. The beam diameter was set to 20  $\mu$ m for the magnetite/wüstite phase and 50  $\mu$ m for the metal and slag phases. The employed standard materials, X-ray lines, and the detection limits obtained for EPMA are listed in Table 2. The obsidian was used for measuring the light element, i.e., the oxygen, in all samples.

At least eight analyzing spots were randomly selected from the wellquenched areas of the copper phase, whereas, for each reported point of magnetite/wüstite and slag phases, three individual spots were measured and subsequently averaged to ensure the homogeneity. It should be noted that two different kinds of magnetite/wüstite crystals were observed in the molten slag phase, i.e., the primary and secondary magnetite/wüstite crystals. The primary magnetite/wüstite, including the bulk continuous layer and the discrete crystals, were stable at high temperature. The discrete primary magnetite/wüstite crystals had a euhedral shape with typical sizes ranging from 10 to 50  $\mu$ m. Whereas the secondary magnetite/wüstite crystals which were formed during quenching displayed dendritic structures with size less than 10  $\mu$ m, shown in Fig. 2(a).

Fig. 2(b) gives an example showing the principle of selecting the individual analyzing spots for both slag and primary magnetite/wüstite phases. As can be seen, the reported value for point 1 from the slag phase was the average of three spots (A, B, and C). Similarly, the reported value for point 2 from the wüstite phase was obtained using the average of three spots (a, b, and c). In this way, at least 24 individual spots were selected for each phase from the areas either without many copper

segregations or secondary magnetite/wüstite crystals.

The use of microanalysis technique ensured the accurate determination of chemically dissolved copper in slags. The phase analyses of magnetite/wüstite and slag were carried out close to each other from the same well-quenched areas. The typical totals of EPMA analyzes results were within 98–100.7 wt%. The raw data were corrected using the online PAP-ZAF matrix correction [26].

#### 3. Results and discussion

The typical microstructures of samples obtained from 1200 to 1300 °C and at different  $P_{O2}$  are illustrated in Fig. 3. The metallic copper-slag-magnetite/wüstite-gas equilibria were observed in all samples obtained in this study. The wüstite and magnetite phases were distinguished by using the atomic ratio of iron to oxygen measured by EPMA. It was regarded as wüstite if the atomic ratio of iron to oxygen was close to 1, and with lower ratio as magnetite. The solid saturation phase of the system (FeO<sub>x</sub>) was dependent on the  $P_{O2}$  at each fixed temperature. For example, the system was saturated with wüstite at 1200–1250 °C and in the  $P_{02}$  range of  $10^{-10}$  to  $10^{-9}$  atm but was saturated with magnetite at higher  $P_{\Omega 2}$ . When temperature was increased further to 1300 °C, the  $P_{\Omega 2}$ range for magnetite saturation narrowed and shifted to higher  $P_{\Omega 2}$  $(\geq 10^{-7}$  atm). It was noted that the molten slag area increased with increasing temperature at a given  $P_{O2}$ . The molten copper alloy was homogenous, whereas copper droplets were entrained and related to the glassy slag phase and magnetite/wüstite solids [27]. Thus, EPMA analyses for the slag phase were conducted from those bigger areas without many copper precipitations, as described at the end of section 2. The experimentally measured equilibrium compositions of copper alloy, slag, and magnetite/wüstite are collected in Table 3. The normalization of the primary results was done by recalculating the total to 100 wt% with their original proportions. The results with significant standard deviations were omitted and were not used for describing the properties of copper alloy and slag.



(a) CE-17, 1250 °C, Po2 of 10<sup>-8</sup> atm

(b) CE-15, 1200 °C, Po2 of 10<sup>-9</sup> atm

**Fig. 2.** Primary and secondary magnetite crystals in slag (a) and the schematic of EPMA analyses for the compositions of slag and wüstite phases (b) conducted for sample CE-15 obtained at 1200 °C and  $P_{O2}$  of 10<sup>-9</sup> atm. Small circles marked with A-C and a-c represent the individual analyzing spots from the molten slag and the solid wüstite phases, respectively.

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(a) CE-32, 1200 °C, *P*<sub>O2</sub> of 10<sup>-10</sup> atm.



(d) CE-20, 1250 °C, P<sub>O2</sub> of 10<sup>-10</sup> atm.

Epoxy

Copper







(e) CE-17, 1250 °C, Po2 of 10<sup>-8</sup> atm.





(c) CE-34, 1200 °C, Po2 of 10<sup>-8</sup> atm.



(f) CE-41, 1250 °C, Po2 of 10<sup>-6.5</sup> atm.





Wüstite

500 µm

(h) CE-27, 1300 °C, P<sub>O2</sub> of 10<sup>-7</sup> atm.

(i) CE-39, 1300 °C, Po2 of 10<sup>-6.5</sup> atm.

Fig. 3. Typical back-scattered images of sample microstructures at 1200–1300 °C and  $P_{O2}$  of  $10^{-10}$  to  $10^{-6.5}$  atm.

3.1. Composition of copper alloy

### 3.1.1. Copper in metal vs $P_{O2}$

Slag

The equilibrium concentrations of copper and iron in the metallic copper alloy measured by EPMA analyses are displayed in Fig. 4. Previous experimental results [16,17,19–21] obtained at silica/Al–Fe spinel saturation containing different trace elements in the equilibrium system were also plotted in the graphs for comparison. Additionally, the computational results at FeO<sub>x</sub> saturation using MTDATA-MTOX database and previous thermodynamic assessment [12] were compared with

the present results.

Fig. 4(a) indicates that the copper concentration in molten alloy phase increased from approximately 97 wt% to around 99 wt% with increasing  $P_{O2}$  at all temperatures investigated in this study, mostly due to the oxidation of iron and minor elements into the slag phase. The temperature had little effect on copper concentration in the metal alloy phase. The present results at FeO<sub>x</sub> saturation generally are higher than the previous observations [16,17,19–21]. The presence of varying concentrations of trace elements in different studies can be considered as the key reason for the inconsistencies between the present study and the

#### Table 3

Measured equilibrium compositions of copper alloy, molten slag, and solid magnetite/wüstite phases at 1200–1300  $^{\circ}$ C and  $P_{O2}$  of 10<sup>-10.0</sup>-10<sup>-6.5</sup> atm.

Sample	Temperature∕ °C	Log <sub>10</sub> P <sub>O2</sub> (atm)	Equilibrium copper alloy composition/ wt%			Equilibrium	Equilibrium molten slag composition/wt%			Equilibrium solid magnetite/wüstite composition/wt%		
			0	Fe	Cu	SiO <sub>2</sub>	"FeO"	Cu <sub>2</sub> O	"FeO"	SiO <sub>2</sub>	Cu	
CE-13	1200	-8.0	$0.32 \ \pm$	$0.02~\pm$	$98.03~\pm$	$29.90 \ \pm$	66.27 $\pm$	3.70 $\pm$	$99.14~\pm$	0.71 $\pm$	$0.12~\pm$	
			0.02	0.00	0.11	2.79	2.57	0.44	0.56	0.52	0.08	
CE-34	1200	-8.0	0.19 $\pm$	0.01 $\pm$	98.42 $\pm$	30.51 $\pm$	63.96 $\pm$	4.34 $\pm$	99.42 $\pm$	0.44 $\pm$	$0.12~\pm$	
			0.01	0.00	0.16	0.31	0.61	0.26	0.14	0.14	0.08	
CE-15	1200	-9.0	0.30 $\pm$	$0.06~\pm$	97.62 $\pm$	$\textbf{22.95} \pm$	73.71 $\pm$	1.98 $\pm$	98.18 $\pm$	1.66 $\pm$	$0.13~\pm$	
			0.01	0.01	0.47	0.16	0.25	0.13	1.38	1.32	0.11	
CE-33	1200	-9.0	$0.19~\pm$	$0.06~\pm$	97.86 $\pm$	$\textbf{23.03} \pm$	74.80 $\pm$	1.45 $\pm$	99.07 $\pm$	$0.89~\pm$	0.03 $\pm$	
			0.01	0.01	0.12	0.64	0.22	0.41	0.07	0.06	0.02	
CE-23	1200	-10.0	0.29 $\pm$	0.29 $\pm$	97.39 $\pm$	$\textbf{21.27} \pm$	75.92 $\pm$	0.85 $\pm$	99.15 $\pm$	0.70 $\pm$	$0.13~\pm$	
			0.01	0.01	0.12	0.37	0.39	0.11	0.04	0.01	0.03	
CE-32	1200	-10.0	0.18 $\pm$	0.26 $\pm$	96.90 $\pm$	$21.36~\pm$	77.93 $\pm$	0.86 $\pm$	99.10 $\pm$	0.76 $\pm$	$0.13~\pm$	
			0.01	0.02	0.08	0.40	0.34	0.15	0.28	0.28	0.02	
CE-26	1250	-6.5	$0.26 \pm$	$0.01~\pm$	99.19 $\pm$	$\textbf{28.18} \pm$	$60.22 \pm$	10.70 $\pm$	99.30 $\pm$	0.42 $\pm$	$0.24~\pm$	
			0.03	0.00	0.17	0.36	0.19	0.29	0.03	0.03	0.01	
CE-41	1250	-6.5	$0.27~\pm$	$0.01~\pm$	99.48 ±	$\textbf{28.17} \pm$	$60.83 \pm$	$9.32 \pm$	99.32 $\pm$	0.41 $\pm$	$0.22 \pm$	
			0.02	0.00	0.03	0.43	0.89	1.30	0.04	0.02	0.02	
CE-16	1250	-7.0	$0.30 \pm$	$0.01 \pm$	98.71 ±	28.04 $\pm$	$65.72 \pm$	5.84 $\pm$	98.81 $\pm$	0.99 ±	$0.17~\pm$	
			0.02	0.00	0.07	0.12	0.65	0.83	1.83	1.73	0.09	
CE-30	1250	-7.0	0.22 +	0.01 +	99.16 +	27.26 +	64.97 +	6.19 +	99.31 +	0.52 +	0.14 +	
			0.01	0.00	0.02	0.37	0.22	0.48	0.08	0.05	0.05	
CE-17	1250	-8.0	0.29 +	0.05 +	98.37 +	21.39 +	75.57 +	2.41 +	99.30 +	0.65 +	0.04 +	
02 1/	1200	010	0.02	0.01	0.04	0.40	0.36	0.39	0.14	0.14	0.02	
CE-29	1250	-8.0	0.22 +	0.05 +	98.70 +	21.55 +	74.56 +	2.49 +	99.26 +	0.71 +	0.03 +	
	1200	0.0	0.01	0.01	0.06	0.27	0.21	0.29	0.03	0.03	0.01	
CF-18	1250	-9.0	0.01	0.19 +	98 17 +	17.99 +	80.98 +	1.26 +	99 18 +	0.60 +	0.19 +	
01 10	1200	5.0	0.03	0.03	0.10	0.16	0.16	0.10	0.02	0.00 ±	0.02	
CE 28	1250	0.0	0.03	0.05	0.10 07 30 ±	19 19 ±	80.34 ±	0.10	00.02	0.65 +	0.12 +	
GE=20	1250	-9.0	0.22 ±	0.19 ±	97.30 ±	10.10 ±	0.42	0.07 ±	99.19 ±	0.03 ±	0.15 ±	
CE 10	1250	10.0	0.02	0.01	0.20	17.20	0.43 91.02 L	0.31	0.03	0.08	0.00	
CE-19	1230	-10.0	$0.31 \pm$	$0.83 \pm$	90.03 ±	$17.29 \pm$	$0.02 \pm$	$0.75 \pm$	99.41 ±	$0.49 \pm$	0.09 ±	
CE 20	1050	10.0	0.01	0.07	0.10	17.40	0.25	0.09	0.02	0.01	0.01	
GE-20	1230	-10.0	$0.20 \pm$	0.78 ±	90.80 ±	17.40 ±	0.65	0.04 ±	99.44 ±	0.40 ±	0.09 ±	
05.00	1000	6.5	0.01	0.01	0.05	0.35	0.05	0.21	0.01	0.01	0.01	
CE-39	1300	-6.5	0.26 ±	0.02 ±	99.37 ±	22.33 ±	/2.14 ±	3.90 ±	99.41 ±	0.48 ±	0.09 ±	
	1000		0.01	0.00	0.04	0.50	0.88	0.85	0.02	0.03	0.02	
CE-21	1300	-7.0	$0.32 \pm$	$0.03 \pm$	98.83 ±	18.90 ±	75.49 ±	3.14 ±	99.43 ±	0.50 ±	0.06 ±	
	1000		0.01	0.02	0.04	0.65	0.71	0.53	0.02	0.01	0.01	
CE-27	1300	-7.0	$0.21 \pm$	$0.02 \pm$	99.11 ±	19.18 ±	$76.51 \pm$	$3.57 \pm$	99.19 ±	$0.66 \pm$	$0.08 \pm$	
			0.02	0.01	0.04	0.93	0.97	0.48	0.28	0.28	0.02	
CE-37	1300	-8.0	$0.20~\pm$	$0.20 \pm$	98.71 $\pm$	$12.53 \pm$	83.77 $\pm$	$2.46 \pm$	99.20 $\pm$	$0.49 \pm$	$0.27 \pm$	
			0.01	0.02	0.03	0.13	0.15	0.17	0.05	0.01	0.05	
CE-38	1300	-8.0	0.21 $\pm$	$0.12 \pm$	99.10 $\pm$	13.16 $\pm$	84.06 $\pm$	$2.26 \pm$	99.18 $\pm$	0.46 $\pm$	$0.32 \pm$	
			0.01	0.01	0.06	0.55	0.41	0.41	0.05	0.01	0.05	

#### literature [16,17,19-21].

In the study by Sukhomlinov et al. [21], the increase of temperature from 1250 to 1350 °C had a slightly decreasing impact on copper concentration in the metal alloy phase in equilibrium with silica-saturated iron silicate slags. Dańczak et al. [16] reported that MgO addition into the Al–Fe spinel saturated iron-silicate slag had a little effect on the copper concentration in the metal phase. The results by Avarmaa et al. [17,19] indicate that CaO addition to the Al–Fe spinel saturated iron silicate slag slightly increased copper concentration in the metal phase. The addition of MgO and CaO into iron silicate slags led to a decrease of FeO activity and a subsequent decrease of iron activity in copper alloy, resulted in an increase of copper concentration in the metal alloy phase.

## 3.1.2. Iron in metal vs $P_{O2}$

As indicated in Fig. 4(b), the concentration of iron in the metal alloy phase decreased over the entire  $P_{O2}$  range investigated in this study, due to its oxidation to the slag phase. The influence of  $P_{O2}$  on the iron concentration in metal gradually decreased at higher  $P_{O2}$ , as reported in previous studies [12,16,17,20,21]. The molten copper equilibrated with iron silicate slag at 1200 °C in the present study exhibited the lowest iron centration, and it was increased with increasing temperature at a given  $P_{O2}$  as reported in the literature [12]. However, the effect of a higher temperature on increasing the iron concentration in the metal phase decreased at the higher  $P_{O2}$  side. Similar impact of temperature on the

iron concentration in metal was also observed by Sukhomlinov et al. [21]. The present results obtained at 1250 °C fitted well with the observations by other researchers [16,17,21]. The iron concentration in metal obtained at 1200–1300 °C and at magnetite/wüstite saturation in the present study were close to the calculated results by MTDATA and Hidayat et al. [12].

## 3.1.3. Oxygen in metal vs P<sub>02</sub>

The concentration of oxygen in the metal alloy phase in equilibrium with magnetite/wüstite-saturated iron silicate slags in the present study are shown in Fig. 4(d). The measured oxygen concentrations were between 0.2 and 0.3 wt% without clear correlation to  $PO_2$ . The modeling results by MTDATA and Hidayat et al. [12] fit well with each other and showed an increasing trend with increasing oxygen partial pressure at all temperatures. The present experimentally measured oxygen concentrations in metal were higher than the calculated results which may ascribe to the formation of oxide layer on the metal surface of the polished section.

## 3.2. Composition of slag

## 3.2.1. Concentration of copper in slag

The concentrations of copper in the slags are shown in Fig. 5 as a function of logarithmic  $P_{O2}$ . The loss of copper in copper smelting



Fig. 4. Copper and iron concentrations in the metal phase at 1200–1300 °C as a function of logarithmic Po2; (a)-copper; (b) and (c)-iron; (d)-oxygen.

processes mainly occurs to the discarded slag after slag cleaning [28], presenting in both physically entrained and chemically dissolved forms in the slags. It can be found that the copper concentration in slag increased with increasing  $P_{02}$  and especially at 1250 °C the trend line was almost exponential indicating to much greater copper concentrations at high  $P_{02}$ , similar to the trends reported [12,16,17,20]. The copper dissolution in slag decreased with increasing temperature at a given  $P_{02}$ , which is due to the higher Fe/SiO<sub>2</sub> ratio in slag at higher temperature [12]. The impact of temperature got stronger at higher  $P_{02}$ . Similar decreasing impact of higher temperature on the copper loss in slags was observed also by Sukhomlinov et al. [21] and Hidayat et al. [12].

The earlier results reported [16,17,20] were close to the present results at 1250 °C. However, the data obtained by Avarmaa et al. [17] from the Al–Fe spinel saturated FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>–CaO slag were slightly lower than the present results at 1250 °C when the  $P_{O2}$  was higher than  $10^{-8}$  atm. The present results obtained at 1300 °C were on the lower side of the observations by Avarmaa et al. [19] and Hidayat et al. [12] when the  $P_{O2}$  was higher than  $10^{-8}$  atm. The calculated copper concentrations in magnetite/wüstite-saturated slags by MTDATA are slightly on the higher side to our experimental results and the computational results by Hidayat et al. [12]. It was found that the additions of basic oxides Al<sub>2</sub>O<sub>3</sub>, MgO, and CaO into the iron silicate slags can effectively decrease copper concentration in the slags [16–21]. Mackey [29] and Keyworth [30] reported that the silicon-oxygen network in iron silicate slags can be depolymerized by Al<sub>2</sub>O<sub>3</sub>, MgO, and CaO additions, leading to a lower

liquidus temperature and slag viscosity, and finally resulting in a decrease of mechanical copper loss in slags. On the other hand, the  $Al^{3+}$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  ions replace part of the copper cations in slags and thus also lower the chemical loss.

#### 3.2.2. Distribution of copper between metal and slag

As suggested by Yazawa et al. [31], the dissolution of copper from metal phase to the molten slag can be expressed using the following reaction equation:

$$[Cu]_{in metal} + \nu/2O_2 = (CuO_\nu)_{in slag}$$
<sup>(2)</sup>

Where the valence of copper in slags equals to  $2\nu$ . The distribution coefficient of copper between metal and slag can be defined as follows:

$$L^{\rm Cu/S}\rm Cu = [\rm Cu]_{\rm in \ metal}/(\rm Cu)_{\rm in \ slag}$$
<sup>(3)</sup>

According to the suggestions by other researchers [32–34], the logarithmic distribution coefficient of copper between metal and slag can be described as:

$$Log_{10}L^{Cu/S}Cu = A - (v/2) \cdot log_{10}P_{O2}$$
 (4)

Where A is a constant at a given temperature. Therefore, the oxidation degree of copper in slags can be obtained based on the slope, i.e.,  $-\nu/2$ , of the fitted relationship between  $\text{Log}_{10}L^{\text{Cu/S}}$ Cu and  $\text{log}_{10}P_{02}$ . The distribution coefficient of copper between metallic copper alloy and magnetite/wüstite saturated iron silicate slag is presented in Fig. 6 as a



Fig. 5. The concentration of copper in slag vs. P<sub>02</sub> obtained in this study compared to previous authors' data at 1200–1300 °C.



**Fig. 6.** Distribution coefficient of copper between metal and magnetite/wüstite saturated iron silicate slags at 1200, 1250 and 1300  $^{\circ}$ C as a function of  $P_{02}$ .

function of  $P_{O2}$  between 1200 and 1300 °C.

It can be observed that the distribution coefficient of copper between metallic copper alloy and slag decreased with increasing  $P_{O2}$  at all temperatures investigated in this study. The decreasing trend can be attributed to the increase of copper oxide in slags with increasing  $P_{O2}$ . The distribution coefficient of copper increased by approximately 0.2 logarithmic unit with increasing temperature from 1200 to 1250 °C. The positive effect of temperature on the distribution coefficient of copper was stronger at  $P_{O2}$  higher than  $10^{-8}$  atm when temperature increased from 1250 to 1300 °C. The slopes of the trend lines at 1200–1250 °C and 1300 °C were approximately -0.3, -0.3 and -0.2, respectively, suggesting that Cu<sup>+</sup> was the predominant valence state in the slags.

### 3.2.3. Activity and activity coefficient of $CuO_{0.5}$ in slag

As indicated in section 3.3, copper was mainly present as monovalent oxide (i.e.,  $CuO_{0.5}$ ) in the present magnetite/wüstite saturated slags. The equilibrium between the metallic copper alloy and copper oxide in slags in controlled CO–CO<sub>2</sub> atmosphere can be expressed further by equation (5), as suggested by Mackey [29]:

$$[Cu(l)]_{in metal} + \frac{1}{2} CO_2(g) = (CuO_{0.5}(l))_{in slag} + \frac{1}{2} CO(g) \Delta G^{\theta} = 68030 - 13.22T/K (J/mol) [34]$$
(5)

The activity of  $CuO_{0.5}$  can be expressed as equation (5), as proposed in literature [29,34] when the alloy is considered as pure, liquid state (*a*Cu = 1):

$$aCuO_{0.5} = K_5 \cdot (CO_2/CO)^{1/2}$$
(6)

Where  $K_5$  denotes to the equilibrium constant of reaction (5). Fig. 7 shows the calculated activity of CuO<sub>0.5</sub> (aCuO<sub>0.5</sub>) and activity coefficient of CuO<sub>0.5</sub> ( $\gamma$ CuO<sub>0.5</sub>) as a function of the present experimentally measured molar fraction of CuO<sub>0.5</sub> (xCuO<sub>0.5</sub>) and Fe/SiO<sub>2</sub> ratio in magnetite/wüstite and copper saturated iron silicate slag.

It can be found that the activity of CuO<sub>0.5</sub> increased with increasing the molar fraction of CuO<sub>0.5</sub> in slags at 1200–1300 °C, similar to the trend reported in literature [9,17,35–39]. The effect of temperature on *a*CuO<sub>0.5</sub> was not so clear, although the results at 1300 °C were on the higher side compared to the results at 1200–1250 °C. The activity of CuO<sub>0.5</sub> obtained in spinel/wüstite-saturated iron silicate slag in the present study is slightly higher than previous results with tridymite-saturated slags [9,35–38], but fits well with the data reported by Hidayat et al. [9] and Avarmaa et al. [17] at spinel/wüstite saturation.

The activity coefficient of  $CuO_{0.5}$  obtained is shown in Fig. 7(b). They varied from 3.8 to 8.8 and displayed similar decreasing trends with increasing activity of  $CuO_{0.5}$  and molar fraction of  $CuO_{0.5}$  in slag, as observed in literature [9,17,35–39]. The present results with spinel/wüstite saturation in slags are on the higher side of the data obtained at tridymite saturation. It was reported by Altman and Kellog [35] as well as Elliott et al. [36] that CaO addition to the silica saturated slags



**Fig. 7.** The activity and activity coefficient of CuO<sub>0.5</sub> in slags at 1200–1300 °C νs. xCuO<sub>0.5</sub> and Fe/SiO<sub>2</sub> ratio in slags (standard state liquid oxide); (a)-*a*CuO<sub>0.5</sub>; (b) and (c)-γCuO<sub>0.5</sub>.

can effectively increase the activity coefficient of  $CuO_{0.5}$  in slags. Similar effect of CaO on the activity coefficient of  $CuO_{0.5}$  in slags was also observed by Avarmaa et al. [17]. The activity coefficient of  $CuO_{0.5}$  in slags displayed an increasing trend with increasing Fe/SiO<sub>2</sub> ratio from approximately 0.5 to 3, after which it decreased at higher Fe/SiO<sub>2</sub> ratio range. Similar increasing trend for the activity coefficient of  $CuO_{0.5}$  in slags as a function of Fe/SiO<sub>2</sub> ratio were also observed by Avarmaa et al. [17] and Hidayat et al. [9].

## 3.2.4. Concentrations of "FeO", SiO2 and Fe/SiO2 ratio in slag

Phase composition measurements by EPMA cannot provide information about the proportion of cations for the elements with varying valencies. For the ease of presentation, the total iron content in the magnetite/wüstite saturated slags in the present study was recalculated as "FeO". Fig. 8 shows the concentrations of "FeO" and SiO<sub>2</sub> as well as the Fe/SiO<sub>2</sub> ratio in slags. The compositions of the molten slag phase with standard deviations ( $\pm 1\sigma$ ) determined at varying conditions are listed in Table 3.

The "FeO" concentration in the present magnetite/wüstite saturated slags had a decreasing trend with increasing  $P_{O2}$  at all temperatures investigated, which may be attributed to the formation of magnetite/wüstite phase which consumed part of the iron. The increase of temperature led to an increase of "FeO" concentration in slags at a given  $P_{O2}$ .

Compared with "FeO" in slags, the concentration of SiO<sub>2</sub> in slags displayed an opposite increasing trend with increasing  $P_{O2}$ . The increase of temperature from 1200 to 1300 °C had a decreasing impact on the "FeO" concentration in slags at a fixed  $P_{O2}$ .

The corresponding Fe/SiO<sub>2</sub> ratio (w/w) decreased with increasing  $P_{O2}$  at all temperatures, as observed by Avarmaa et al. [17–19]. However, the decreasing trend was steeper at 1300 °C. The Fe/SiO<sub>2</sub> ratio increased by approximately one unit with increasing temperature from 1200 to 1250 °C, whereas, when increasing temperature from 1250 to 1300 °C, the ratio was at  $P_{O2} 10^{-8}$  atm 1.5 times higher and decreased to one time higher (ratio) at  $P_{O2} 10^{-6.5}$ . The present experimental results for Fe/SiO<sub>2</sub> ratio obtained at magnetite/wüstite saturation were somewhat lower than the computational MTDATA results at all temperatures investigated and somewhat higher at wüstite saturation to the results by Hidayat et al. [12]. The experimental results at magnetite saturation fit well the computational results using FactSage [12].

#### 3.3. Concentration of copper in magnetite/wüstite

Fig. 9 shows that varying concentrations (approximately 0.03–0.4 wt %) of copper dissolved into the solid magnetite/wüstite phases. The copper concentration in tridymite was too low to be detected by EPMA in our previous studies [18,21,22] focusing on the



Fig. 8. Concentrations of "FeO" (a), SiO<sub>2</sub> (b) and Fe/SiO<sub>2</sub> ratio (c) and (d) in the magnetite/wüstite and metallic copper saturated slags as a function of P<sub>O2</sub>.



Fig. 9. Concentration of copper in magnetite/wüstite.

copper/slag/tridymite/gas equilibrium system, whereas in the copper/slag/Al–Fe spinel/gas equilibrium systems copper was measured in the solid Al–Fe spinel [16,19,20]. The computational results for copper in magnetite using MTDATA agreed with the present

results and the previous calculated data by Hidayat et al. [12]. Instead, the present experimentally measured copper concentration in wüstite at low oxygen partial pressures were much lower when compared to the assessment by Hidayat et al. [12].

## 3.4. Spinel and wüstite liquidus

As varying concentrations of copper dissolved into the slag, the magnetite/wüstite saturated iron silicate slag in equilibrium with metallic copper in this study conforms to the ternary  $FeO_x$ -SiO<sub>2</sub>-CuO<sub>x</sub> system. The experimentally measured liquid slag compositions were plotted onto the quasi-binary phase diagrams of the  $FeO_x$ -SiO<sub>2</sub>-CuO<sub>x</sub> system at spinel (Fe<sub>3</sub>O<sub>4</sub>) and liquid copper saturation at 1200–1300 °C, respectively, as shown in Figs. 10–12. In spite of the variable oxygen partial pressure, the diagram is thermodynamically consistent under the given constraints.

The MTDATA (version 7.2) thermodynamic software [40,41] with its MTOX database (version 8.2) [41] was used for calculating the isothermal quasi-binary FeO<sub>x</sub>-SiO<sub>2</sub>-CuO<sub>x</sub> phase diagrams at the same conditions, *i.e.*, at solid iron oxide and liquid copper saturation, as in the experiments. The isotherms were calculated using a combination of FeO and Fe<sub>2</sub>O<sub>3</sub> as the terminal iron oxide phase. The data by Hidayat et al. [9] were recalculated to correspond "FeO" as the iron oxide dissolved in the slag. The discontinuities in the calculated phase boundaries at 1200–1250 °C represent the location of the four-phase field of Cu



**Fig. 10.** A comparison of present results and those obtained by Hidayat et al. [9] and Sineva et al. [14] at 1200 °C with the thermodynamic calculation by MTDATA at spinel (i.e., magnetite in the present study)-Cu(l) saturation: Hidayat et al. [9] +; Sineva et al. [14]  $\odot$ ; and this study  $\Delta$ ; — MTDATA phase boundary; note the kink (*i.e.*, the v-shape) at low Cu<sub>2</sub>O concentrations indicating the FeO-Fe<sub>3</sub>O<sub>4</sub> double saturation. The solid saturation phase is marked with squares in the figure.



**Fig. 11.** A comparison of the experimental results obtained at 1250 °C with the thermodynamic calculation by MTDATA: Hidayat et al. [9]  $\times$ ; Sineva et al. [14] +; and this study  $\odot$ ; red line (–) shows the calculated phase boundary. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 12.** A comparison of the experimental results obtained at 1300 °C with the thermodynamic calculation by MTDATA: Hidayat et al. [9]  $\times$ ; this study  $\Delta$ ; the computational phase boundary is shown as red line (–). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(l)-slag-magnetite-SiO<sub>2</sub>(s) at each temperature.

It can be observed that the present experimental results obtained at 1200–1300 °C deviate significantly (2–5 wt% in terms of SiO<sub>2</sub>) from the predictions by MTDATA and the discrepancies increased at higher copper oxide concentrations (i.e., at higher oxygen partial pressures). Compared with the predictions by MTDATA using the MTOX database [41], the present experimentally measured molten slag-magnetite/-wüstite phase boundaries at all temperatures investigated show lower Cu<sub>2</sub>O concentrations and higher SiO<sub>2</sub> concentrations. The predictions by MTDATA were executed for 'pure' FeO<sub>x</sub>-SiO<sub>2</sub>-CuO<sub>x</sub> systems with the prevailing constraints in the experiments, whereas additional minor elements existed in the present study with low concentrations [25].

The experimental points at FeO saturation are much closer to the calculated ones than those at  $Fe_3O_4$  saturation. The results by Hidayat et al. [9] and Sineva et al. [14] are close to the present result at low oxygen partial pressures. Here one special feature in previous data is that most points by Hidayat et al. [9] were obtained in inert atmosphere without control of the oxygen partial pressure. Thus, their accuracy at high Cu<sub>2</sub>O concentrations may be questionable.

#### 4. Conclusions

The phase equilibria between metallic copper and magnetite/wüstite saturated iron silicate slags were experimentally investigated at 1200–1300 °C and  $P_{O2}$  of  $10^{-10}$  to  $10^{-6.5}$  atm. The high-temperature isothermal equilibration experiments were conducted in magnetite/wüstite crucibles in controlled CO–CO<sub>2</sub> atmospheres followed by quenching and direct phase analysis by EPMA. The experimental technique used in this study ensured the accuracies of determining the compositions for each phase without any systematic errors in sample preparation.

The removal of iron from the metallic copper alloy can be increased by increasing the oxygen partial pressure and lowering temperature. Copper dissolution in the slag increased with increasing  $P_{O2}$  and decreasing temperature. The equilibrium iron concentration and the Fe/SiO<sub>2</sub> ratio of the magnetite/wüstite saturated iron silicate slags decreased with increasing  $P_{O2}$  and decreasing temperature. The obtained spinel saturation data for the slag phase were in good agreement with the experimental studies of Hidayat et al. [9] and Sineva et al. [14].

Some discrepancies were observed between the present experimentally measured magnetite/wüstite-molten slag phase boundary results and thermodynamic predictions by MTDATA and Factsage [12]. The calculated copper solubility in wüstite by Hidayat et al. [12] contradicted with the present experimental results and the computational results using MTDATA deviated somewhat from the experimental results of Fe/SiO<sub>2</sub> ratio in slags. The present experimental results together with Hidayat et al. [9] and Sineva et al. [14] suggest that the SiO<sub>2</sub>-spinel (magnetite) double saturation in the presence of metallic copper locates at higher SiO<sub>2</sub> concentrations in the slag than the MTDATA predictions.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

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