Phase Equilibria Studies of the Cu-Fe-O-Si System in Equilibrium with Air and with Metallic Copper

TAUFIQ HIDAYAT, HECTOR M. HENAO, PETER C. HAYES, and EVGUENI JAK

Phase equilibria of the Cu-Fe-O-Si system have been investigated in equilibrium: (1) with air atmosphere at temperatures between 1373 K and 1673 K (1100 °C and 1400 °C) and (2) with metallic copper at temperatures between 1373 K and 1573 K (1100 °C and 1300 °C). High-temperature equilibration/quenching/electron-probe X-ray microanalysis (EPMA) techniques have been used to accurately determine the compositions of the phases in equilibrium in the system. The new experimental results are presented in the form of "Cu_2O"-"Fe_2O_3"-SiO_2 ternary sections. The relationships between the activity of $CuO_{0.5(l)}$ and the composition of slag in equilibrium with metallic copper are discussed. The phase equilibria information of the Cu-Fe-O-Si system is of practical importance for industrial copper production processes and for the improvement of the existing thermodynamic database of copper-containing slag systems.

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I. INTRODUCTION

THE separation of iron from the copper-rich phase (matte or blister copper) during the high-temperature copper production processes takes place through the formation of molten slag predominantly containing iron oxide and silica with appreciable amounts of copper and other impurities, such as, CaO, MgO, and Al_2O_3. The copper in the slag can be in the form of mechanically trapped copper-rich phase or chemically dissolved copper species. Detailed information on the phase equilibria of the Cu-Fe-O-Si system is essential to understand the latter.

Only a few experimental studies on the phase equilibria of the Cu-Fe-O-Si slag system can be found in the literature. Ruddle *et al.*[1] used silica crucibles to study the copper solubility in iron silicate slag in equilibrium with pure Cu over a wide range of oxygen partial pressures. Altman and Kellogg[2] and Elliot *et al.*[3] investigated the solubility of copper in iron silicate slag equilibrated with Cu-Au alloy in silica crucibles at controlled oxygen partial pressures and temperatures. Taylor and Jeffes[4] employed a levitation technique to investigate the equilibria between fully liquid iron silicate slag and Cu-Au alloy at various Fe/Si ratios in the slag, several temperatures and oxygen partial pressures. Oishi *et al.*[5] measured the oxygen partial pressures of Cu-Fe-O-Si slags equilibrated with pure Cu in silica crucibles at various temperatures using a solid electrolyte galvanic cell technique. These previous studies are restricted only to the phase equilibria of the slags at reducing conditions where copper metal or copper alloy is present; most of them are limited to the phase equilibria of tridymite-saturated slags.

The current study focuses on the phase equilibria of the systems in equilibrium: (1) with air at temperatures between 1373 K and 1673 K (1100 °C and 1400 °C) and (2) with metallic copper at temperatures between 1373 K and 1573 K (1100 °C and 1300 °C). The selected systems and conditions are relevant to those of industrial copper production process. The new experimental results also provide further information required for the improvement of the existing thermodynamic databases of copper-containing slag systems.

II. EXPERIMENTAL TECHNIQUE AND PROCEDURE

A. *Experimental Procedure and Sample Examination*

Details of the experimental procedure and apparatus have been described in a previous publication by the authors.[6] Initial mixtures were made by mixing high-purity oxide powders of SiO_2 (99.99 wt pct purity), Fe_2O_3 powder (99.99 wt pct purity), Cu_2O powder (99.99 wt pct purity), and CuO powder (99.3+ wt pct purity) (supplied by Alfa Aesar, Ward Hill, MA). For experiments in equilibrium with metallic copper, Cu powder (99.7 wt pct purity; supplied by Alfa Aesar) was added 30 wt pct in excess of the mass of the oxide mixture to ensure metallic copper present at the final equilibrium. The initial compositions of the mixtures were selected such that at equilibrium there would be liquid slag in equilibrium with one or more crystal phases. Less than 0.3 g mixture was used in each equilibration experiment.

A platinum envelope (10 mm × 12 mm) made from 0.025 mm-thick Pt foil was used for equilibration in air. For experiments in equilibrium with metallic copper, both quartz crucibles and spinel envelopes were used.

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The quartz (SiO_2) crucible was made from high-purity silica rod, which was fused at a high temperature into a crucible shape with diameter of 13 mm and depth of 5 mm. The spinel (Fe_3O_4) container was prepared from 99.5 wt pct pure iron foil with thickness of 0.1 mm, which was folded to an envelope shape (10 mm × 12 mm) and oxidized for 1 hour at 1573 K (1300 °C) at an oxygen partial pressure of 10^{-6} atm.

All equilibration experiments were carried out in a vertical reaction tube (impervious recrystallized alumina, 30 mm inner diameter) within an electrical resistance silicon carbide (SiC) heated furnace. A working thermocouple in a recrystallized alumina sheath was placed immediately next to the sample to monitor the actual sample temperature. The working thermocouple was periodically calibrated against a standard thermocouple (supplied by the National Measurement Institute of Australia, New South Wales, Australia). The overall absolute temperature accuracy of the experiment was estimated to be ±3 K.

An open system reaction tube was used for equilibration of the sample with air. In the case of experiments in equilibrium with metallic copper, an inert atmosphere of high-purity argon gas (99.999 pct purity; supplied by Coregas, New South Wales, Australia) in a gas-tight system was selected. In some cases, the equilibration of slag with metallic copper was undertaken at controlled oxygen partial pressures by introducing a stream of $CO\text{-}CO_2\text{-}Ar$ gas. A total of 5 pct and 20 pct CO diluted in high-purity argon (beta standards with ±0.02 pct uncertainty; supplied by BOC, Queensland, Australia) and high-purity CO_2 (99.995 pct pure; supplied by Coregas, New South Wales, Australia) were used to create low CO/CO_2 ratios in the gas stream resulting oxygen partial pressures of 10^{-5} atm and 10^{-8} atm. The oxygen partial pressures were confirmed by an oxygen probe made of a yttria-stabilized zirconia solid electrolyte cell ($SiRO_2$, DS-type oxygen probe; Australian Oxytrol Systems, Victoria, Australia) and were found to be within the accuracy of the DS-type oxygen probe, *i.e.*, ±0.1 Log (p_{O_2}) units.[7]

The sample was suspended in the hot zone of the furnace by a platinum support wire (0.5 mm diameter). Thirty minutes of premelting at 25 K above the equilibration temperature was conducted, followed by equilibration at the final target temperature and atmosphere condition for required equilibration period. At the end of the equilibration process, the sample was rapidly quenched in cold water saturated with sodium chloride. The specimen was then washed thoroughly in water before being dried on a hot plate, mounted in epoxy resin, and cross-sectioned by using conventional metallographic polishing techniques.

The polished sections of the samples were carbon coated and the phase compositions were measured using an electron-probe X-ray microanalysis (EPMA) technique with wavelength dispersive detectors (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). The EPMA was operated under 15 kV accelerating voltage and 15 nA probe current with Duncumb–Philibert atomic number, absorption, and fluorescence correction (ZAF correction). $CaSiO_3$, Fe_2O_3 (supplied by Charles M. Taylor Co., Stanford, CA), and Cu_2O (supplied by Structure Probe Inc. Supplies, West Chester, PA) standards were used for calibration of the EPMA. The concentrations of metal cations were measured with EPMA; no information on the different oxidation states of the cations was obtained. All copper oxide and iron oxide concentrations were recalculated as Cu_2O and Fe_2O_3, respectively, for presentation purposes only. This corresponds to projecting the actual phase compositions in the Cu-Fe-O-Si tetrahedron onto the $Cu_2O\text{-}Fe_2O_3\text{-}SiO_2$ plane as shown in Figure 1.

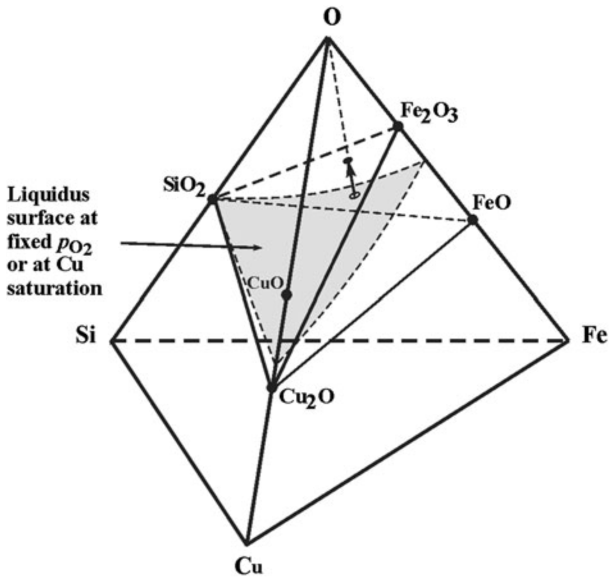

Fig. 1—Compositional space in the Cu-Fe-O-Si system and projection onto the $Cu_2O\text{-}Fe_2O_3\text{-}SiO_2$ plane.

A homogeneous, glassy phase was readily formed on quenching of the slags containing low Cu_2O concentrations. The compositions of the liquid and the crystal phases were measured by EPMA point analysis method. In the case of slags with high Cu_2O concentration, the glassy homogeneous areas were limited to locations at the surfaces directly contacting the quenching medium. The criteria for performing an accurate, repeatable, and objective measurement by the EPMA line analysis method described by Nikolic *et al.*[8] was applied to obtain the average compositions of the liquid phase.

B. *Confirmation of Achievement of Equilibrium*

To ensure the achievement of equilibrium in the samples, several measures were used including: (1) approaching the final equilibrium point from two different starting compositions, (2) variation of equilibration time, (3) assessment of the compositional homogeneity of the phases by EPMA, and (4) consideration of specific reactions that may hinder the achievement of equilibrium. Several dedicated sets of experiments were carried out for these purposes, and part of the results are given in Table I as an example.

Similar to the previous studies on the "Cu_2O"-"Fe_2O_3" system with metallic copper[8,9] and in the "Cu_2O"-SiO_2 systems in air and with metallic copper,[6] the equilibration of the Cu-Fe-O-Si systems can be approached from different directions: (1) from a more reducing condition by introducing copper oxide in the initial mixture in the form of Cu_2O and (2) from a more oxidizing condition by introducing copper oxide in the initial mixture in the form of CuO.

Different holding times of 12 hours and 24 hours were tested for equilibration of the "Cu_2O"-"Fe_2O_3"-SiO_2 slag under air atmosphere, whereas holding times of 6 hours and 12 hours were tested for the equilibration of "Cu_2O"-"Fe_2O_3"-SiO_2 slag with metallic copper (Table I). It can be observed in Table I that all of the final compositions of the solid and liquid phases are within 0.5 wt pct of the average values, which means that the shortest holding time in each condition is adequate for the achievement of the final equilibrium point. From this set of experiments, it was decided that equilibration experiments in the air atmosphere should be carried out for minimum equilibration periods of 12 hours. For the system in equilibrium with metallic copper, the minimum equilibration period was selected to be 6 hours. In some cases where the equilibration temperature was higher than the temperatures listed in Table I, equilibration with metallic copper was undertaken at a shorter equilibration time of 4 hours.

The achievement of equilibrium in the silicate slag systems in equilibrium with metallic copper at fixed oxygen partial pressure has been tested by Henao *et al.*[10] It was reported that 12 hours holding time was sufficient to attain equilibrium. An equilibration period of 24 hours was selected in the current study to ensure the achievement of equilibrium between slag, metallic copper, and gas phase.

III. RESULTS AND DISCUSSION

A. *Liquidus in the "Cu_2O"-"Fe_2O_3"-SiO_2 System in Equilibrium with Air*

A micrograph of a quenched "Cu_2O"-"Fe_2O_3"-SiO_2 slag produced by equilibration in air atmosphere is provided in Figure 2. The primary phase crystals that can be found in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with air atmosphere are tridymite, cuprite, spinel, and delafossite. Extensive measurements in air have been carried out only in the tridymite primary phase field at temperatures between 1373 K and 1673 K (1100 °C and 1400 °C), and the results are reported in Table II.

The liquidus surface presented in Figure 3 shows that the liquidus isotherms in the tridymite primary phase field are almost parallel to the "Cu_2O"-"Fe_2O_3" join. The liquidus isotherms in the spinel primary phase field are estimated based on the measured tridymite-spinel (Fe_3O_4) boundary points and data in the "Cu_2O"-"Fe_2O_3" binary phase diagram in air.[11] The spinel-delafossite, cuprite-delafossite, and cuprite-tridymite boundary phase fields, indicated by bold dashed lines,

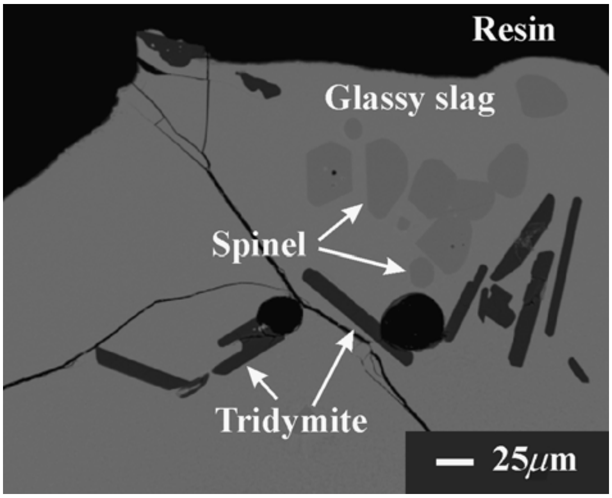

Fig. 2—Backscattered scanning electron micrograph of quenched slag in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with air in the presence of spinel ("Fe_3O_4") and tridymite (SiO_2) crystals.

Table I. Equilibration of "Cu_2O"-"Fe_2O_3"–SiO_2 Systems in Air and with Metallic Copper

			Slag Composition (wt pct)		
Temperature [K (°C)]	Equilibration Time (h)	Phase	SiO_2	"Cu_2O"	"Fe_2O_3"
Equilibration Conditions →	In Equilibrium with Air				
1373 (1100)	12	liquid	12.4	64.9	22.7
		spinel	0.1	24.5	75.4
		tridymite	98.5	0.9	0.6
1373 (1100)	24	liquid	12.4	63.8	23.7
		spinel	0.1	24.4	75.5
		tridymite	98.6	0.9	0.5
Equilibration Conditions →	In Equilibrium with Metallic Cu				
1423 (1150)	6	liquid	17.0	50.8	32.2
		spinel	0.1	4.7	95.2
		tridymite	98.9	0.6	0.5
1423 (1150)	12	liquid	16.4	51.7	31.9
		spinel	0.1	4.0	95.9
		tridymite	98.9	0.6	0.5

Spinel iron oxide concentration is reported as Fe_2O_3 because of the selected projection of the actual "Cu_2O"-FeO-Fe_2O_3-SiO_2 composition to the Cu_2O-Fe_2O_3-SiO_2 plane.

Table II. Experimentally Determined Phase Compositions for the “Cu_2O”-“Fe_2O_3”-SiO_2 System in Equilibrium with Air

Temperature [K (°C)]	Equilibration Time (h)	Phase	SiO_2 (wt pct)	“Cu_2O” (wt pct)	“Fe_2O_3” (wt pct)
1373 (1100)	12	liquid	12.4	64.9	22.7
		spinel	0.1	24.5	75.4
		tridymite	98.5	0.9	0.6
1373 (1100)	24	liquid	12.4	63.8	23.7
		spinel	0.1	24.4	75.5
		tridymite	98.6	0.9	0.5
1373 (1100)	24	liquid	12.8	71.9	15.3
		tridymite	98.6	1.1	0.3
1373 (1100)	24	liquid	13.5	78.3	8.2
		tridymite	98.5	1.4	0.1
1423 (1150)	24	liquid	13.4	65.1	21.5
		tridymite	98.8	0.7	0.5
1423 (1150)	12	liquid	13.9	74.2	11.9
		tridymite	98.8	1.0	0.2
1473 (1200)	12	liquid	13.9	51.1	35.0
		spinel	0.1	18.8	81.1
		tridymite	98.9	0.5	0.6
1473 (1200)	12	liquid	15.4	64.1	20.5
		tridymite	98.8	0.9	0.3
1473 (1200)	12	liquid	15.2	72.8	12.0
		tridymite	98.8	1.0	0.2
1523 (1250)	12	liquid	14.9	41.5	43.6
		spinel	0.1	15.5	84.4
		tridymite	99.1	0.5	0.4
1523 (1250)	12	liquid	17.2	52.9	29.9
		tridymite	99.1	0.6	0.3
1523 (1250)	12	liquid	18.3	69.5	12.2
		tridymite	98.9	0.9	0.2
1573 (1300)	12	liquid	14.2	34.5	51.3
		spinel	0.1	13.2	86.7
		tridymite	99.1	0.4	0.5
1573 (1300)	12	liquid	19.1	53.8	27.1
		tridymite	99.1	0.6	0.3
1573 (1300)	12	liquid	15.2	35.1	49.7
		tridymite	99.1	0.4	0.5
1573 (1300)	12	liquid	19.0	54.0	27.0
		tridymite	99.2	0.5	0.3
1623 (1350)	12	liquid	15.5	23.3	61.2
		spinel	0.1	9.1	90.8
		tridymite	98.9	0.1	1.0
1623 (1350)	12	liquid	15.3	22.7	62.0
		spinel	0.1	9.9	90.0
		tridymite	99.0	0.2	0.8
1623 (1350)	12	liquid	21.2	60.1	18.7
		tridymite	99.1	0.7	0.2
1673 (1400)	12	liquid	16.3	14.8	68.9
		spinel	0.1	6.2	94.7
		tridymite	99.1	0.1	0.8
1673 (1400)	12	liquid	19.3	29.4	51.3
		tridymite	99.2	0.3	0.5
1673 (1400)	12	liquid	22.5	72.0	5.5
		tridymite		Solid was not measured	
1673 (1400)	12	liquid	23.9	70.6	5.5
		tridymite		Solid was not measured	
1673 (1400)	12	liquid	23.2	58.4	18.4
		tridymite	99.1	0.8	0.1

Spinel iron oxide concentration is reported as Fe_2O_3 because of the selected projection of the actual “Cu_2O”-FeO-Fe_2O_3-SiO_2 composition to the Cu_2O-Fe_2O_3-SiO_2 plane.

are approximations based on the data of the respective binary systems in air.[6,11] The ternary eutectic point between cuprite, delafossite, and tridymite is estimated to be at 1313 ± 10 K (1040 °C) with composition of approximately 70 wt pct “Cu_2O”, 20 wt pct “Fe_2O_3”, and 10 wt pct SiO_2.

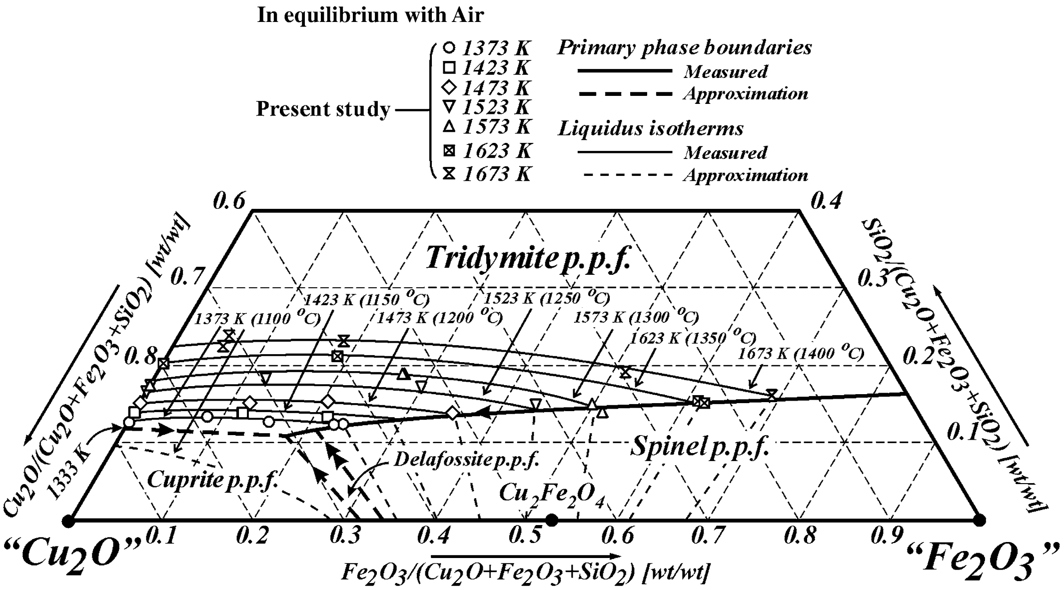

Fig. 3—Liquidus isotherms in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with air (p_{O_2} = 0.21 atm) (data points in the pseudobinary "Cu_2O"-SiO_2 are from Hidayat *et al.*[6] and "Cu_2O"-"Fe_2O_3" are from Yamaguchi[11]).

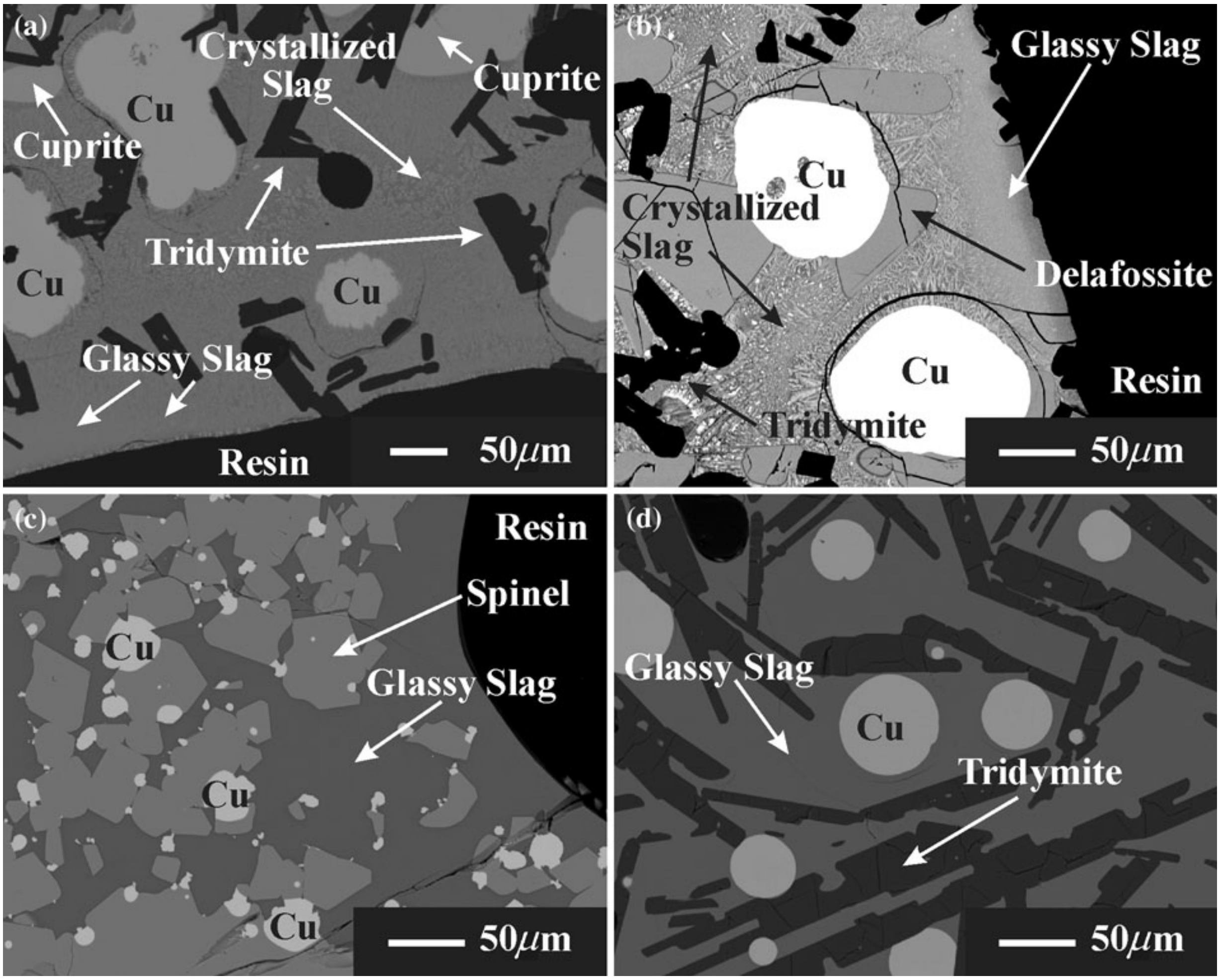

Fig. 4—Backscattered scanning electron micrographs of the quenched liquid slags in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper in the presence of: (*a*) cuprite-Cu_2O + tridymite-SiO_2, (*b*) delafossite-$Cu_2Fe_2O_4$ + tridymite-SiO_2, (*c*) spinel-"Fe_3O_4", and (*d*) tridymite-SiO_2.

Table III. Experimentally Determined Phase Compositions for the "Cu_2O"-"Fe_2O_3"-SiO_2 System in Equilibrium with Metallic Copper

Temperature [K (°C)]	Equilibration Time (h)	Phase	SiO_2 (wt pct)	"Cu_2O" (wt pct)	"Fe_2O_3" (wt pct)
1373 (1100)	12	liquid	13.1	62.5	24.4
		delafossite	0.0	46.1	53.9
		tridymite	98.5	1.1	0.4
1373 (1100)	12	liquid	9.4	68.1	22.5
		cuprite	0.0	99.5	0.5
		delafossite	0.0	46.3	53.7
1373 (1100)	12	liquid	12.4	68.2	19.4
		cuprite	0.0	99.6	0.4
		tridymite	98.5	1.3	0.2
1373 (1100)	12	liquid	12.7	68.0	19.3
		cuprite	0.0	99.5	0.5
		tridymite	98.5	1.3	0.2
1373 (1100)	12	liquid	12.5	65.2	22.3
		tridymite	98.4	1.1	0.5
1423 (1150)	24	liquid	7.2	62.6	30.2
		spinel	0.1	5.5	94.4
1423 (1150)	6	liquid	17.0	50.8	32.2
		spinel	0.1	4.7	95.2
		tridymite	98.9	0.6	0.5
1423 (1150)	12	liquid	16.4	51.7	31.9
		spinel	0.1	4.0	95.9
		tridymite	98.9	0.6	0.5
1423 (1150)	12	liquid	14.8	60.9	24.3
		tridymite	98.6	1.0	0.4
1423 (1150)	6	liquid	12.5	78.1	9.4
		cuprite	0.0	99.9	0.1
		tridymite	98.8	1.0	0.2
1473 (1200)	12	liquid	8.7	57.0	34.3
		spinel	0.1	3.6	96.3
1473 (1200)	6	liquid	13.5	47.3	39.2
		spinel	0.1	3.2	96.7
1473 (1200)	6	liquid	12.6	47.7	39.7
		spinel	0.1	3.1	96.8
1473 (1200)	6	liquid	18.5	42.5	39.0
		spinel	0.1	2.7	97.2
		tridymite	98.9	0.5	0.6
1473 (1200)	6	liquid	17.7	53.2	29.1
		tridymite	98.8	0.7	0.5
1473 (1200)	4	liquid	16.5	61.4	22.1
		tridymite	98.7	0.9	0.4
1473 (1200)	12	liquid	15.5	69.0	15.5
		tridymite	98.8	0.9	0.3
1523 (1250)	12	liquid	13.5	40.3	46.2
		spinel	0.1	2.3	97.6
1523 (1250)	24	liquid	22.8	27.6	49.6
		spinel	0.1	1.9	98.0
1523 (1250)	6	liquid	25.1	22.6	52.3
		spinel	0.3	0.8	98.9
		tridymite	99.1	0.2	0.7
1523 (1250)	6	liquid	22.9	31.9	45.2
		tridymite	99.0	0.4	0.6
1523 (1250)	6	liquid	21.9	40.9	37.2
		tridymite	98.9	0.6	0.5
1523 (1250)	6	liquid	18.4	57.9	23.7
		tridymite	98.8	0.8	0.4
1523 (1250)	6	liquid	15.6	1.8	82.6
		spinel	0.5	0.1	99.4
1523 (1250)	24	liquid	20.4	2.0	77.6
		spinel	0.6	0.1	99.3
1523 (1250)	24	liquid	25.3	6.3	68.4
		spinel	0.5	0.1	99.4
1523 (1250)	24	liquid	35.2	1.3	63.5

Table III. Continued

Temperature [K (°C)]	Equilibration Time (h)	Phase	SiO_2 (wt pct)	"Cu_2O" (wt pct)	"Fe_2O_3" (wt pct)
		tridymite	99.2	0.0	0.8
1523 (1250)	24	liquid	32.8	3.1	64.1
		tridymite	99.0	0.2	0.8
1523 (1250)	24	liquid	30.4	6.0	63.6
		tridymite	99.0	0.2	0.8
1523 (1250)	12	liquid	28.3	11.7	60.0
		tridymite	99.1	0.2	0.7
1573 (1300) (p_{O_2} = 10^{-5} atm)	24	liquid	20.9	21.6	57.5
		spinel	0.2	1.0	98.8
1573 (1300) (p_{O_2} = 10^{-6} atm)	24	liquid	22.5	9.2	68.3
		spinel	0.3	0.3	99.4
1573 (1300) (p_{O_2} = 10^{-7} atm)	24	liquid	20.7	2.8	76.5
		spinel	0.5	0.0	99.5
1573 (1300) (p_{O_2} = 10^{-8} atm)	24	liquid	12.5	1.2	86.3
		wustite	0.4	0.4	99.2
1573 (1300)	4	liquid	18.2	68.7	13.1
		tridymite	99.0	0.8	0.2
1573 (1300)	6	liquid	23.3	43.5	33.2
		tridymite	99.1	0.5	0.4
1573 (1300)	12	liquid	27.1	27.0	45.9
		tridymite	99.0	0.4	0.6
1573 (1300)	6	liquid	28.0	21.3	50.7
		tridymite	99.2	0.3	0.5
1573 (1300) (p_{O_2} = 10^{-5} atm)	24	liquid	26.4	23.1	50.5
		tridymite	99.4	0.2	0.4
1573 (1300) (p_{O_2} = 10^{-6} atm)	24	liquid	30.1	10.6	59.3
		tridymite	99.2	0.3	0.5
1573 (1300) (p_{O_2} = 10^{-6} atm)	12	liquid	30.6	10.7	58.7
		tridymite	99.2	0.3	0.5
1573 (1300) (p_{O_2} = 10^{-7} atm)	12	liquid	33.5	5.4	61.1
		tridymite	99.1	0.3	0.6
1573 (1300) (p_{O_2} = 10^{-8} atm)	24	liquid	34.5	2.8	62.7
		tridymite	99.3	0.0	0.7
1573 (1300) (p_{O_2} = 10^{-8} atm)	24	liquid	34.9	2.6	62.5
		tridymite	99.3	0.0	0.7

Spinel iron oxide concentration is reported as Fe_2O_3 because of the selected projection of the actual "Cu_2O"-FeO-Fe_2O_3-SiO_2 composition to the Cu_2O-Fe_2O_3-SiO_2 plane.

B. *Liquidus in the "Cu_2O"-"Fe_2O_3"-SiO_2 System in Equilibrium with Metallic Copper*

Figure 4 shows back-scattered electron micrographs of quenched samples from equilibration experiments with metallic copper. Figure 4(a) shows cuprite (Cu_2O) crystal with round shape morphology. Delafossite ($Cu_2Fe_2O_4$) crystals in Figure 4(b) and spinel ("Fe_3O_4") crystals in Figure 4(c) have similar cubic morphologies. The plate-like tridymite (SiO_2) crystals can be easily identified as shown in Figure 4(d).

Table III provides the measured compositions of the phases in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper. Most of the liquidus points were obtained from experiments undertaken in an inert atmosphere under an argon gas stream. Some liquidus points at 1573 K (1300 °C) were acquired from experiments at controlled oxygen partial pressures between 10^{-5} atm and 10^{-8} atm. The data in Table III, together with information from pseudobinary "Cu_2O"-"Fe_2O_3"[8,9] and "Cu_2O"-SiO_2[6] systems in equilibrium with metallic copper, were used to construct the pseudoternary "Cu_2O"-"Fe_2O_3"-SiO_2 diagram in equilibrium with metallic copper as shown in Figure 5. Previous data reported by Ruddle *et al.*[1] and Oishi *et al.*[5] are indicated by cross and plus symbols, respectively.

The tridymite, cuprite, spinel, and delafossite primary phase fields were identified between 1373 K and 1573 K (1100 °C and 1300 °C). The delafossite-cuprite, spinel-delafossite, and cuprite-tridymite phase boundaries in Figure 5 are approximations based on the information on the "Cu_2O"-"Fe_2O_3"[8,9] and "Cu_2O"-SiO_2[6] pseudobinary systems in equilibrium with metallic copper. The spinel and tridymite boundary line has been determined experimentally.

A narrow, fully liquid area is present at 1373 K (1100 °C) and is surrounded by cuprite, tridymite, and delafossite primary phase fields. Above 1423 K (1150 °C), delafossite is not present and the liquid region is bounded by cuprite, tridymite, and spinel primary phase fields. At 1523 K (1250 °C), two fully liquid areas exist: (1) in the region with high copper

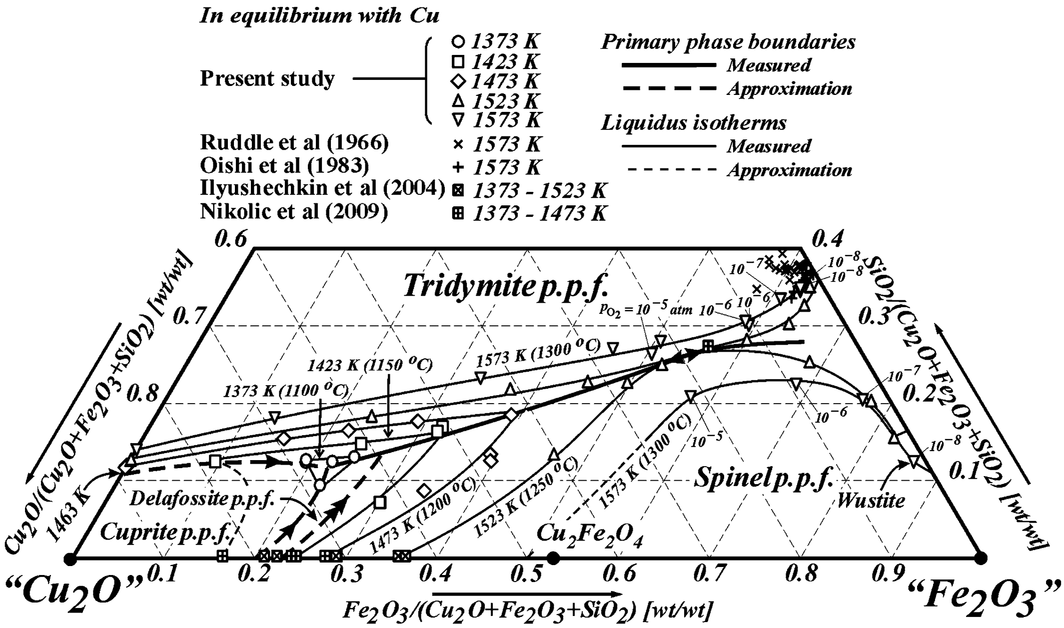

Fig. 5—Liquidus isotherms in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper-iron alloy (data points in the pseudobinary "Cu_2O"-SiO_2 in equilibrium with metallic copper and in the pseudobinary "Fe_2O_3"-SiO_2 in equilibrium with metallic iron are from Hidayat *et al.*[6] and FactSage,[12] respectively. p_{O_2} in atm).

oxide concentration above 25 wt pct "Cu_2O" and (2) in the region with low copper oxide concentration, separated by a region of coexistence of slag, copper, spinel, and tridymite. The two separated fully liquid areas merge at a temperature above 1523 K (1250 °C). In Figure 5, a continuous fully liquid region extending from the "Cu_2O" corner toward "Fe_2O_3"-SiO_2 pseudobinary is present at 1573 K (1300 °C). It can be observed that the liquidus in the tridymite primary phase field at 1573 K (1300 °C) obtained by the current study at copper oxide concentration below 5 wt pct "Cu_2O" is in general agreement with data from the measurements by Oishi *et al.*[5]

It is worth noting that, as the composition of the slag moves away from the "Cu_2O" corner and approaches the "Fe_2O_3"-SiO_2 binary, the oxygen partial pressure of the system decreases. For instance, a decrease in the "Cu_2O" concentration in the spinel liquidus at 1573 K (1300 °C) from 21.6 wt pct to 2.8 wt pct corresponds to a decrease in the oxygen partial pressure of the system from 10^{-5} atm to 10^{-7} atm.

C. *Activity of $CuO_{0.5(l)}$ in the "Cu_2O"-"Fe_2O_3"-SiO_2 Slag in Equilibrium with Metallic Copper*

The dissolution of Cu in the slag at controlled oxygen partial pressures can be analyzed thermodynamically based on the following oxidation reaction:

$$Cu_{(\text{liquid})} + {}^1\!/\!_4\, O_{2(\text{gas})} \leftrightarrow CuO_{0.5(\text{liquid})} \qquad [1]$$

from which the following relationship can be obtained:

$$\begin{aligned} K_{\text{eq}} &= a_{\text{CuO}_{0.5}} \Big/ \left(a_{\text{Cu}} \times p_{O_2}^{1/4} \right) \\ &= \left(\gamma_{\text{CuO}_{0.5}} \times N_{\text{CuO}_{0.5}} \right) \Big/ \left(a_{\text{Cu}} \times p_{O_2}^{1/4} \right) \qquad [2] \end{aligned}$$

where K_{eq} is the equilibrium constant for the oxidation reaction of copper into monometallic copper oxide; $a_{\text{CuO}_{0.5}}$, $\gamma_{\text{CuO}_{0.5}}$ and $N_{\text{CuO}_{0.5}}$ denote the activity of $CuO_{0.5}$ (pure $CuO_{0.5(l)}$ standard state), activity coefficient of $CuO_{0.5}$, and the molar fraction of $CuO_{0.5}$ in the slag phase, respectively; and a_{Cu} is the activity of metallic copper (pure $Cu_{(l)}$ standard state).

The activity of liquid $CuO_{0.5}$ in the "Cu_2O"-"Fe_2O_3"-SiO_2 slag equilibrated with metallic Cu or Cu alloy at 1573 K (1300°C) at controlled oxygen partial pressures in the current study and previous data[1–5] are calculated and compared. K_{eq} = 7.73 at 1573 K (1300 °C) for Reaction [1] is taken from the FactSage[12] database. The activity of copper (a_{Cu}) of the current study is assumed to be unity (only low concentrations of Fe in Cu were measured with EPMA). The calculated activities and activity coefficients of $CuO_{0.5}$ as a function of $N_{\text{CuO}_{0.5}}$ of previous and current studies are presented in Figure 6 showing similar trends. The $CuO_{0.5}$ activity coefficient varies between 2.0 and 6.0, and the $CuO_{0.5}$ component in the slag exhibits a positive deviation from the behavior of an ideal solution.

Subsequent analyses of the current data have been carried out in relation to the location of oxygen isobars and isoactivity coefficient lines of $CuO_{0.5(l)}$ in the "Cu_2O"-"Fe_2O_3"-SiO_2 slag in equilibrium with metallic copper. It can be observed in Figure 7(a) that the oxygen isobars lie almost parallel to the "Fe_2O_3"-SiO_2 join. The 10^{-7} atm and 10^{-8} atm oxygen isobars are located relatively close to the "Fe_2O_3"-SiO_2 join. The Cu_2O concentration difference between the two is less than 3.0 wt pct. The 10^{-5} atm and 10^{-6} atm oxygen isobars are located further from the "Fe_2O_3"-SiO_2 join, at significantly higher copper concentrations.

The $CuO_{0.5(l)}$ isoactivity coefficient lines, in Figure 7(b), indicated by dashed lines, are approximations showing that the $CuO_{0.5(l)}$ activity coefficient increases as the slag composition becomes closer to the "Fe_2O_3"-SiO_2 join; it then reaches a constant value at low copper concentrations exhibiting Henrian behavior.

Figure 8 shows the relationship between the activity coefficient of $CuO_{0.5}$ and the oxygen partial pressure. It can be clearly observed that at the same oxygen partial pressure, the liquid in the spinel primary phase field has higher activity coefficient of $CuO_{0.5}$ than that in the tridymite primary phase field. This tendency suggests that at given oxygen partial pressure and smelting temperature, lower copper solubility in the slag would be achieved if the smelting operation is carried out at spinel saturation.

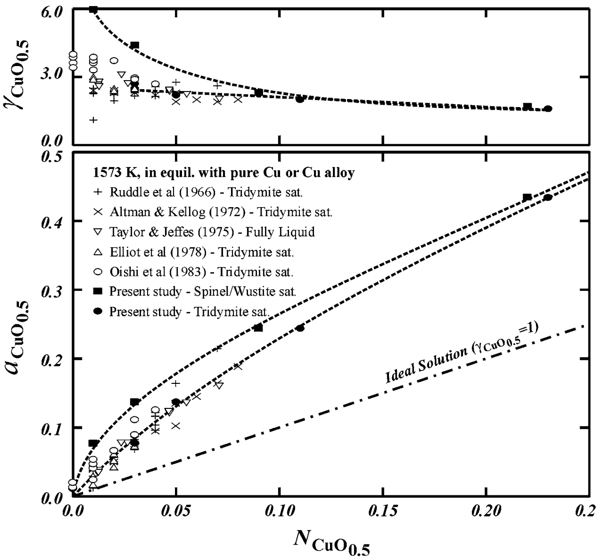

Fig. 6—Activities and activity coefficients of liquid $CuO_{0.5}$ (pure $CuO_{0.5(l)}$ standard state) in Cu-Fe-O-Si slags equilibrated with metallic copper or copper alloy at 1573 K (1300 °C) as a function of molar fraction of $CuO_{0.5}$.

D. *Solid Solutions in the "Cu_2O"-"Fe_2O_3"-SiO_2 Systems in Equilibrium with Air and with Metallic Copper*

The compositions of tridymite crystals in the "Cu_2O"-"Fe_2O_3"-SiO_2 slags at equilibrium with air are provided in Figure 9. Tridymite dissolves measurable amounts of "Cu_2O" and "Fe_2O_3". At 1373 K (1100 °C), the total

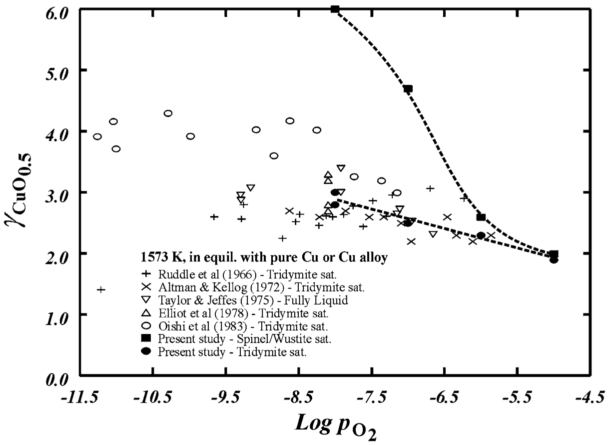

Fig. 8—Activity coefficients of liquid $CuO_{0.5}$ (pure $CuO_{0.5(l)}$ standard state) in the slag equilibrated with metallic copper or copper alloy at 1573 K (1300 °C) as a function of logarithmic value of oxygen potential (p_{O_2} in atm).

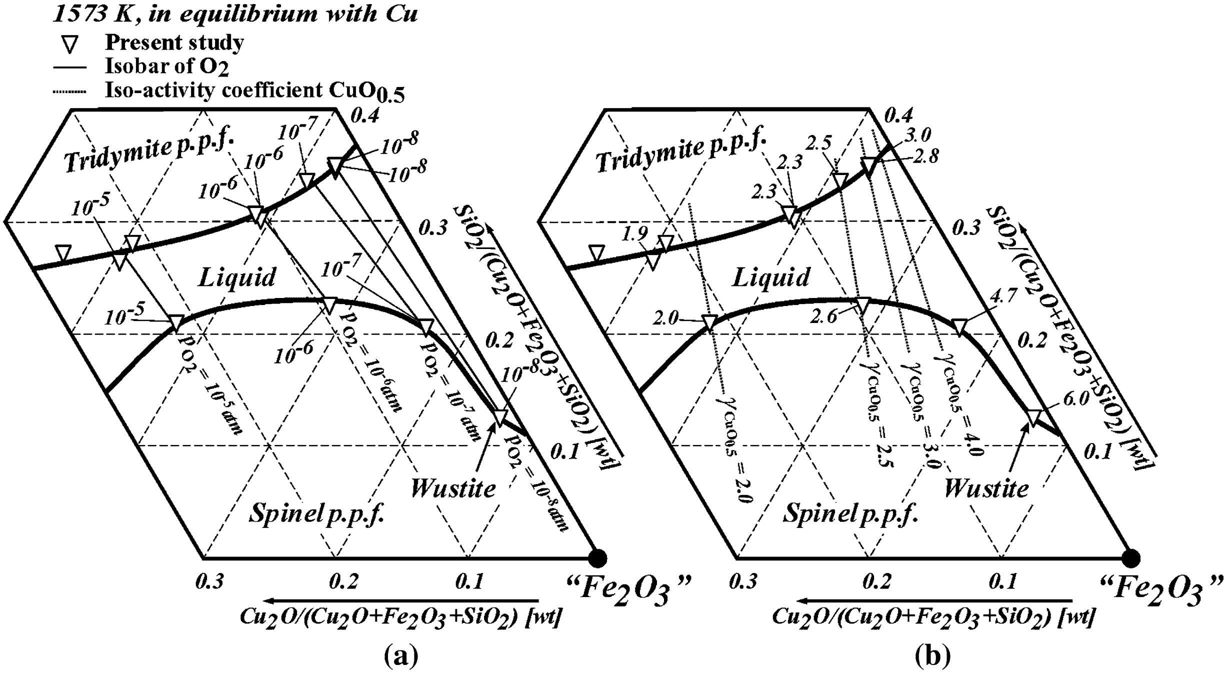

Fig. 7—A section of the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper at 1573 K (1300 °C) showing: (*a*) O_2 isobars (atm) and (*b*) lines of isoactivity coefficient of $CuO_{0.5}$ (pure $CuO_{0.5(l)}$ standard state).

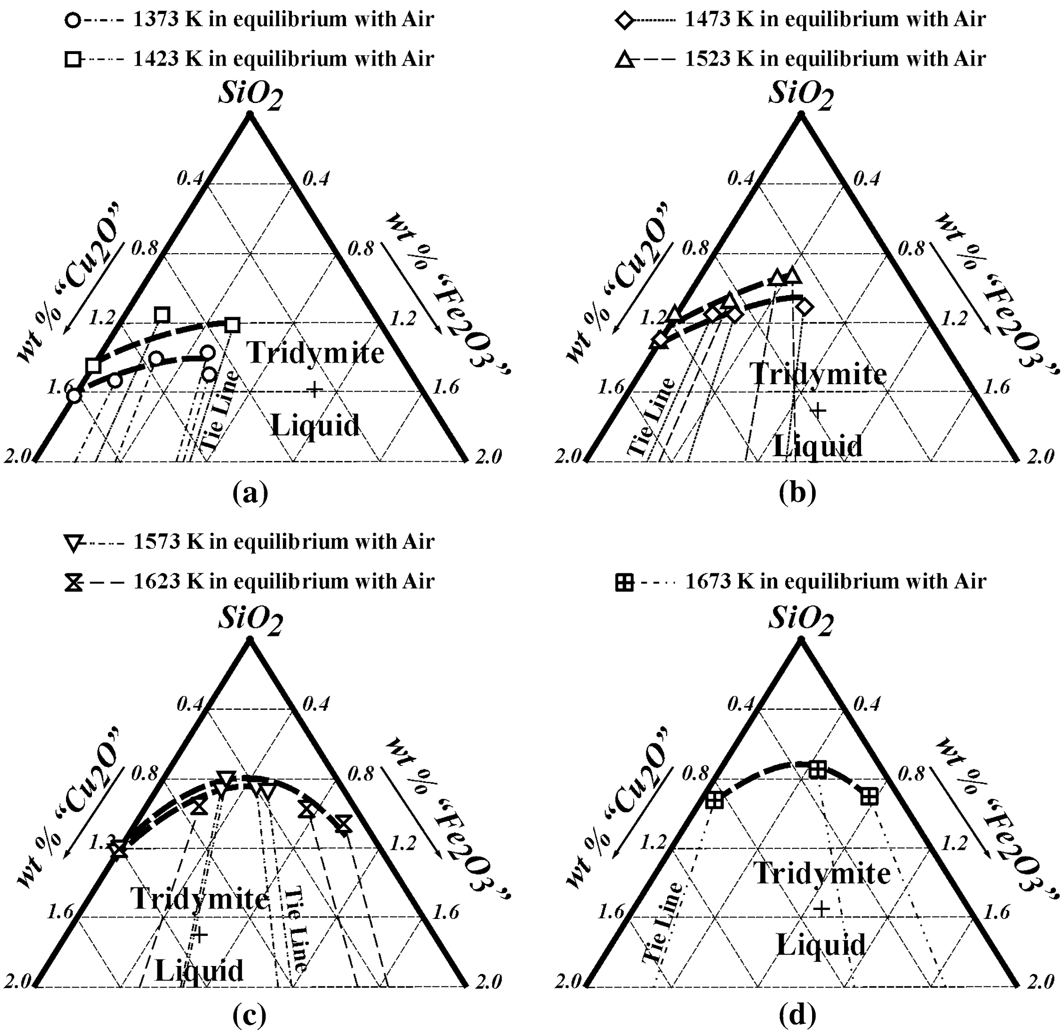

Fig. 9—Tridymite compositions and tie lines to the corresponding liquidus compositions in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with air at: (*a*) 1373 K and 1423 K (1100 °C and 1150 °C), (*b*) 1473 K and 1523 K (1200 °C and 1250 °C), (*c*) 1573 K and 1623 K (1300 °C and 1350 °C), and (*d*) 1673 K (1400 °C) (data points in the pseudobinary "Cu_2O"-SiO_2 are from Hidayat *et al.*[6]).

concentration of solutes ("Cu_2O" + "Fe_2O_3") in tridymite is approximately 1.5 wt pct (Figure 9(a)). Increasing the temperature decreases the concentration of solutes in the tridymite. For example, increasing the temperature from 1373 K to 1523 K (1100 °C to 1250 °C) decreases the total concentration of solutes in tridymite from 1.5 wt pct "Cu_2O" + "Fe_2O_3" to approximately 1 wt pct "Cu_2O" + "Fe_2O_3" (Figures 9(a) and (b)).

The ratio of "Cu_2O" and "Fe_2O_3" in the liquid slag determines the concentration of solutes in the tridymite. It can be observed from Figures 9(c) and (d) that as the "Cu_2O"/"Fe_2O_3" ratio in the liquid slag is increased, the concentrations of solutes in the tridymite crystal go through a minimum value which then increase again. At temperature above 1673 K (1400 °C), the maximum solutes concentration in tridymite crystal is expected to be found at the "Fe_2O_3"-SiO_2 join.

The spinel compositions in equilibrium with tridymite crystal, liquid slag, and air are provided in Table II. The concentrations of silica in spinel crystal in air are below 0.1 wt pct SiO_2. The concentrations of copper oxide in the spinel crystals in air, in contrast, are significant ranging between 6.2 wt pct and 24 wt pct "Cu_2O". The concentrations of copper oxide in spinel crystals in equilibrium with air decrease with increasing temperature. For instance, the concentration of copper oxide decreases from 18.8 wt pct "Cu_2O" to 13.2 wt pct "Cu_2O" when the temperature is increased from 1473 K to 1573 K (1200 °C and 1300 °C).

The concentrations of various solids in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper are given in Table III. It can be observed that cuprite crystal dissolves only "Fe_2O_3"; the concentration of SiO_2 in cuprite is negligible. The concentration of iron oxide in cuprite is approximately 0.45 wt pct "Fe_2O_3" at 1373 K (1100 °C) and decreases to approximately 0.1 wt pct "Fe_2O_3" at 1423 K (1150 °C). There are only a few data on delafossite in the current study. The current measurements show that delafossite does not dissolve SiO_2. The composition of delafossite in equilibrium with metallic copper does not vary significantly and is always close to the composition of stoichiometric Cu_2O-Fe_2O_3.

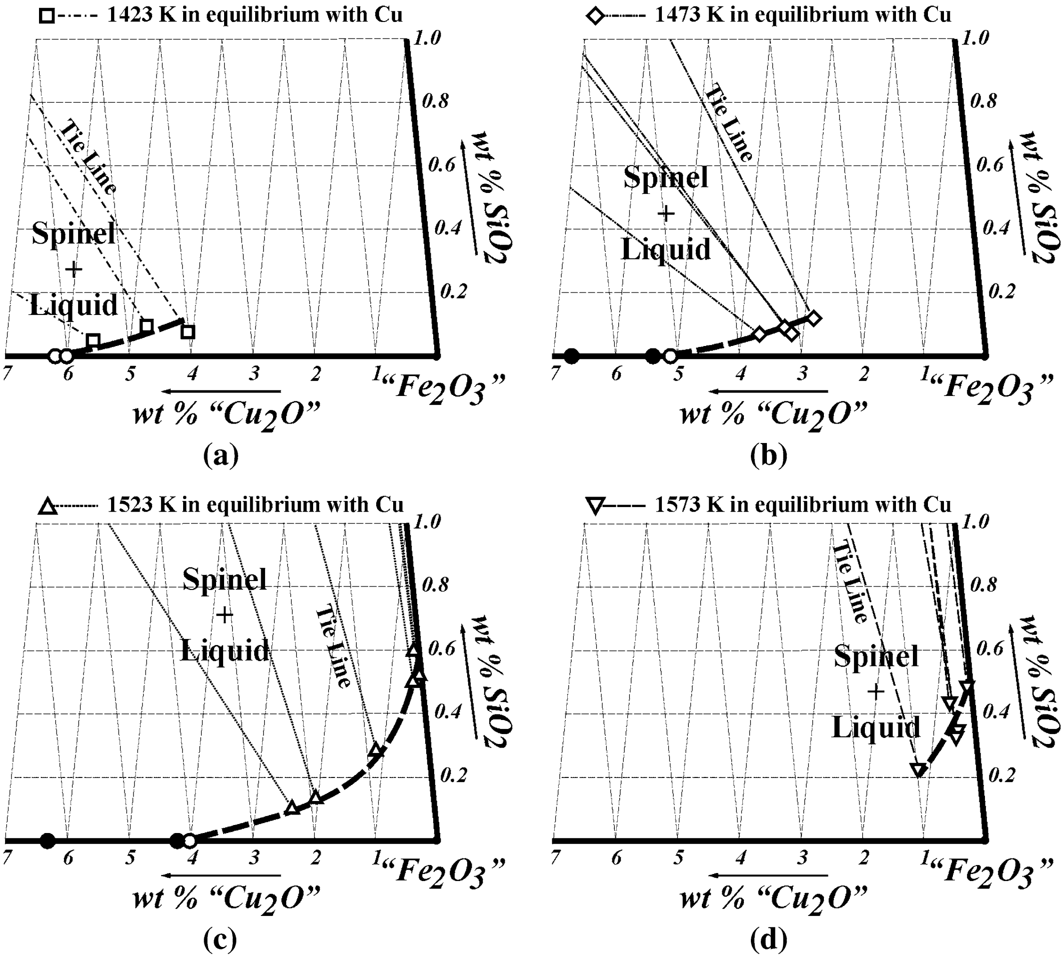

Fig. 10—Spinel compositions and tie lines to the corresponding liquidus compositions in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper at: (*a*) 1423 K (1150 °C), (*b*) 1473 K (1200 °C), (*c*) 1523 K (1250 °C), and (*d*) 1573 K (1300 °C) (data points in the pseudo-binary "Cu_2O"-"Fe_2O_3" are from Ilyusheckin *et al.*[9] (closed circles) and Nikolic *et al.*[8] (open circles)).

The spinel compositions of the "Cu_2O"-"Fe_2O_3"-SiO_2 slags in equilibrium with metallic copper are summarized in Figure 10. Both "Cu_2O" and SiO_2 are found in the spinel solid solutions. The concentrations of solutes ("Cu_2O" and SiO_2) in the spinel solid solution decrease with the increasing temperature. The maximum "Cu_2O" concentration in spinel crystal is reached when slag does not contain SiO_2. When the SiO_2 concentration in the slag increases the "Cu_2O" concentration in spinel gradually decreases, while the SiO_2 concentration in spinel gradually increases. The SiO_2 concentration in the spinel reaches a maximum value when the liquid slag contains small amount of "Cu_2O" as can be observed in Figures 10(c) and (d).

Information on the tridymite solid solutions in the "Cu_2O"-Fe_2O_3"-SiO_2 system in equilibrium with metallic copper is provided in Figure 11. Tridymite crystal takes in measurable amounts of "Cu_2O" and "Fe_2O_3". It is apparent from Figure 11 that when the temperature is increased, the concentrations of "Cu_2O" and "Fe_2O_3" in the tridymite crystal decrease noticeably. The capacity of tridymite to dissolve solutes decreases when liquid slag contains less copper oxide. For example, tridymite takes in more than 1.2 wt pct of solutes ("Cu_2O" + "Fe_2O_3") at 1523 K (1250 °C) when liquid slag contains 57.9 wt pct "Cu_2O". When the liquid slag contains less than 1.3 wt pct "Cu_2O", the tridymite can only dissolve less than 0.8 wt pct of solutes ("Cu_2O" + "Fe_2O_3").

IV. CONCLUSIONS

New phase equilibria information on the "Cu_2O"-"Fe_2O_3"-SiO_2 systems has been obtained in air and in equilibrium with metallic copper. In equilibrium with air, extensive measurements have been carried out to locate the liquidus isotherms of the tridymite primary phase field at various temperatures between 1373 K and 1673 K (1100 °C and 1400 °C). In equilibrium with metallic copper, liquidus isotherms of various primary phase fields have been characterized at temperatures between 1373 K and 1573 K (1100 °C and 1300 °C). The compositions of solid solutions in the systems at the two conditions have been determined and discussed. The

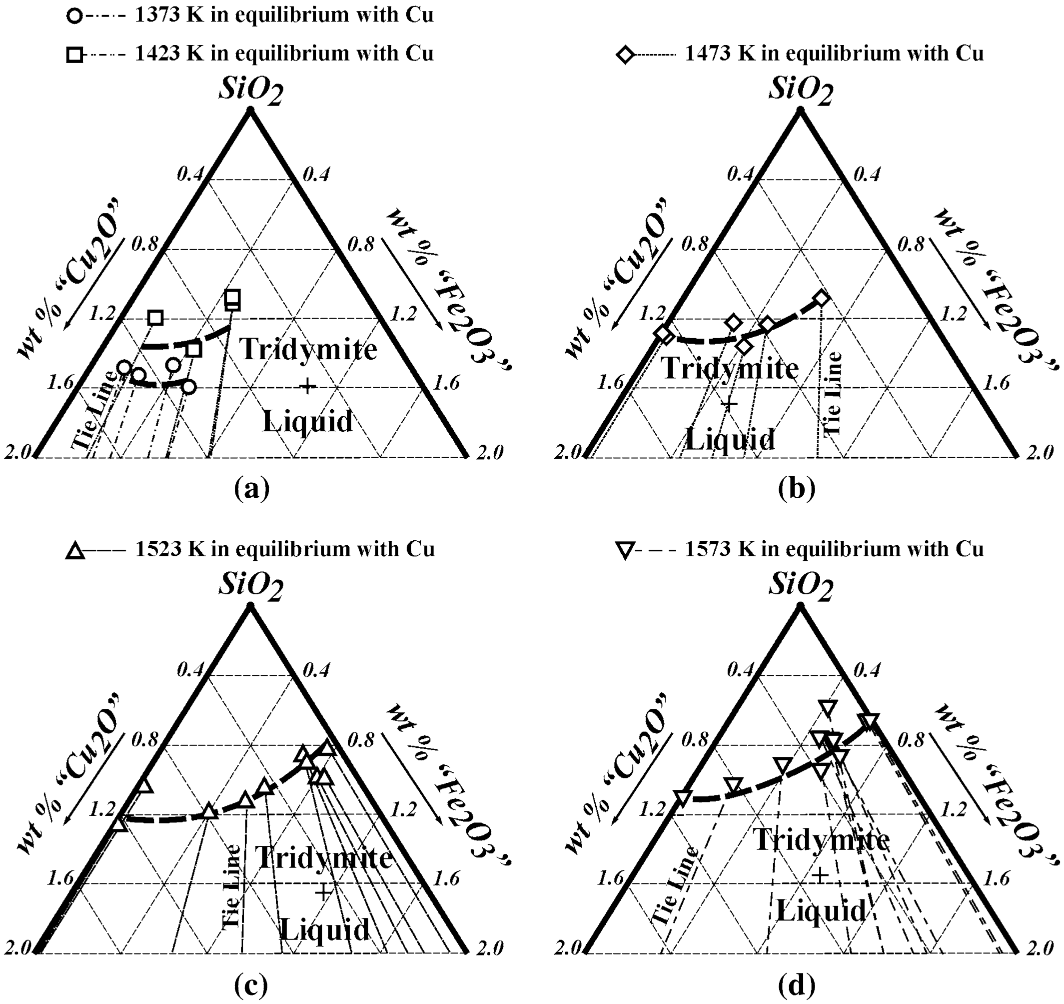

Fig. 11—Tridymite compositions and tie lines to the corresponding liquidus compositions in the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper at: (*a*) 1373 K and 1423 K (1100 °C and 1150 °C), (*b*) 1473 K (1200 °C), (*c*) 1523 K (1250 °C), and (*d*) 1573 K (1300 °C) (data points in the pseudobinary "Cu_2O"-SiO_2 are from Hidayat *et al.*[6]).

phase equilibria information provided by the current study can be used for refinement of the existing thermodynamic databases of copper-containing slag systems and has direct practical implication for industrial copper making processes, in particular for the direct-to-blister copper process, the copper converting process, and the copper refining process.

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