PHASE EQUILIBRIA OF FAYALITE-BASED SLAGS FOR THE SLAG CLEANING PROCESS IN COPPER PRODUCTION

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ABSTRACT

Limited data are available on the phase chemistry of the multi-component slag system at intermediate oxygen partial pressures used in the copper smelting, converting and slag cleaning processes. Recently experimental procedures have been developed and have been successfully applied to characterise a number of complex industrial slags. The experimental procedures involve high temperature equilibration and quenching followed by the electron probe X-ray microanalysis. This technique has been used to construct the phase equilibrium diagram for the "Cu_2O*"-FeO-*Fe_2O_3*-*SiO_2*-CaO-MgO-*Al_2O_3* slag system at controlled oxygen partial pressure and metallic copper saturation conditions, in the range of compositions and temperatures directly relevant to the Slag Cleaning Electric Furnace. The liquidus temperatures in the tridymite and spinel primary phase fields at metallic copper saturation were measured for the fayalite-based slag with 2 wt% of CaO, 0.5 wt% of MgO and 4.0 wt% of *Al_2O_3*.*

In this paper, the experimental technique is explained in detail. The new experimental equilibrium results are presented in the form of the liquidus temperature vs. Fe/SiO_2* phase diagram. The application of the results to the practical operation of the slag cleaning furnace is discussed. The experimental results are compared with the FactSage model predictions.*

INTRODUCTION

Optimal control of the slag chemistry in the copper smelting and converting is one of the important issues influencing efficient and stable operation. Improvements of the copper industrial processes require detailed knowledge of the slag properties. Extensive experimental information regarding the equilibrium between metallic copper and FeO-Fe_2O_3-CaO-SiO_2 in a magnesium crucible at 1573 K and oxygen partial pressures between 10^{-11} to 10^{-4} atm. was reported by Takeda [1]. However, despite its industrial importance, the phase equilibrium at intermediate oxygen partial pressures in the ferrous calcium silicate system at metallic copper saturation has not been fully investigated.

Recently experimental procedures have been developed and have been successfully applied to characterise a number of complex industrial slags. The experimental procedures involve high temperature equilibration and quenching followed by the electron probe X-ray microanalysis. This technique has been used previously by the PYROSEARCH Centre at the University of Queensland to construct the phase equilibrium diagram for the Cu_2O-FeO-Fe_2O_3-SiO_2 slag system at controlled oxygen partial pressure and metallic copper saturation at the conditions relevant to the copper converting slag system [2, 3, 4, 5].

In the present work the experimental technique has been further extended and applied to characterise a range of compositions, temperatures and oxygen partial pressures directly relevant to a copper smelting and copper slag cleaning process within the multi-component system of Cu_2O-FeO-SiO_2-CaO-MgO-Al_2O_3. The target liquidus composition of 2 wt% of CaO, 0.5 wt% of MgO and 4.0 wt% of Al_2O_3 and the range of temperatures from 1150 to 1350°C were investigated. The liquidus at the oxygen partial pressure of $P_{O2}=10^{-8.5}$ atm in equilibrium with metallic copper has been measured using the primary phase suspension technique. In addition, the Cu_2O solubilities in the slag at fixed oxygen partial pressure in equilibrium with metallic copper have also been measured.

In this paper, the obtained experimental equilibrium results are presented in the form of customised phase diagrams as the liquidus temperatures vs Fe/SiO_2. Application of new experimental results in copper slag cleaning process is discussed. New results are compared to the FactSage model predictions.

EXPERIMENTAL TECHNIQUE AND PROCEDURE

There are a number of difficulties in obtaining accurate chemical equilibrium data for complex slag systems in a controlled laboratory environment. Experimental procedures have been developed by the authors and applied to study a number of complex slags used in copper industry [2, 3, 4, 5].

The experimental technique for phase equilibrium measurements is based on the high temperature equilibration of the synthetic slag samples in precisely controlled gas atmosphere and temperature (±2°C) followed up by a rapid quenching procedure. The experimental technique can be readily explained with reference to Figures 1 and 2. The sample is held inside the furnace on a spinel or silica primary phase substrate at a given oxygen partial pressure and temperature. The slag is equilibrated together with the metal phase by adding 100 μm copper powder to the mixture. Under these conditions liquid oxide of composition *a* (see Figure 1) and primary oxide phase of composition c are formed in addition to the metallic copper. The sample is kept for a time sufficient to reach equilibrium and quenched. The equilibration time is specifically tested in the course of the study by extending time, by approaching equilibrium from different directions, and by analysing homogeneity of compositions of phases in final samples. The liquid slag phase is converted into glass on quenching, and the crystalline solids (if present) and metal phases are frozen in place. The quenched sample is then mounted, polished, and the compositions of the liquid and solid phases are measured by the electron probe X-ray microanalysis technique (EPMA). When more than two phases are formed in a multi-component system, all equilibrium phases included metal (if formed) is measured by EPMA in a similar way and the proper diagram is constructed using that information.

The oxygen partial pressure is controlled by flowing CO and CO_2 gas mixtures, and the PO_2 value at a given temperature is calculated by using FactSage [6].

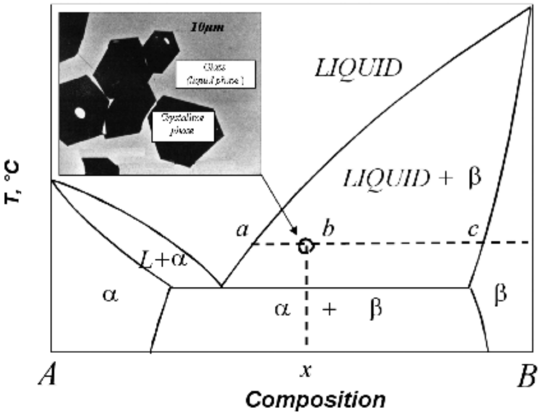

Figure 1: Schematic of approach to phase equilibrium determination using sub-liquidus equilibration, quenching and EPMA

The spinel (Fe_3O_4) substrate was prepared from 99.85 wt% pure iron foil folded into the shape indicated in Figure 2. The silica substrate was prepared from a slice of high purity silica rod. The starting mixtures were made of CaO, SiO_2, Fe_2O_3, MgO, Al_2O_3, Cu_2O and Cu powders. The mixtures, selected for each sample were pelletized and placed into the substrate (spinel or silica). The substrates were supported by platinum wire within the furnace. Special care was taken to avoid the contact of the mixture with the platinum wire and to ensure that the final compositions of slag and metal are free from contamination. Particular attention was given to the substrate/ sample /support configuration design to ensure that the molten slag was held outside of the primary phase substrate by surface tension forces. The open substrate was used to ensure that the liquid slag is the first material to be contacted with the quenching medium thereby achieving the faster quenching rate.

After a holding time of 24 hours at a given temperature and at the oxygen partial pressure of $10^{-8.5}$ atm, the sample was quenched in water with ice. Analysis of the composition of the various phases within the sample was undertaken using a JEOL 8200L (trademark of Japan Electron Optics Ltd., Tokyo) electron microprobe analyzer (EPMA) with wavelength dispersive detectors (WDDs). An acceleration voltage of 15 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with the JEOL 8200L probe was applied. The standards (Charles M. Taylor, Stanford, CA) that were used in the EPMA measurements were as follows: wollastonite ($CaSiO_3$) for Si and Ca, hematite (Fe_2O_3) for Fe, chalcopyrite ($CuFeS_2$) for Cu, MgO for Mg and Al_2O_3 for Al. The compositions were measured to the accuracy within 1 wt%.

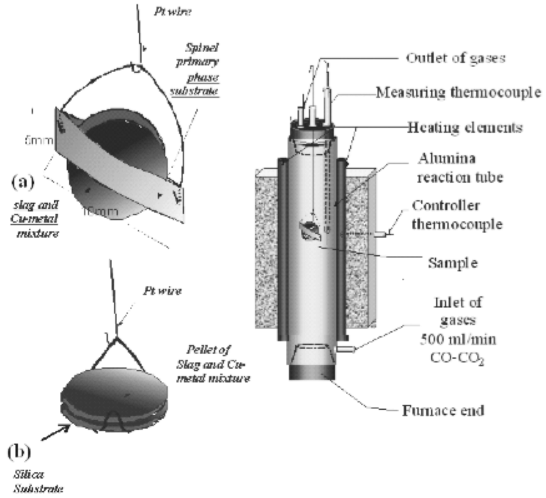

Figure 2: Schematic experimental apparatus with substrates of (a) spinel and (b) silica

EXPERIMENTAL RESULTS

The microstructures observed in the quenched samples at the equilibrium condition between liquid/spinel/metallic copper and liquid/tridymite/metallic copper are presented in Figure 3.

The present study shown that the precipitated iron oxides have a significant amount of other components included Mg, Al, Cu, Ca and Si. In order to keep consistence with other publications [2, 3, 4, 5] as well as FactSage, in the present work the iron oxide phase is referred as spinel, with the understanding that in other sources it is referred as magnetite.

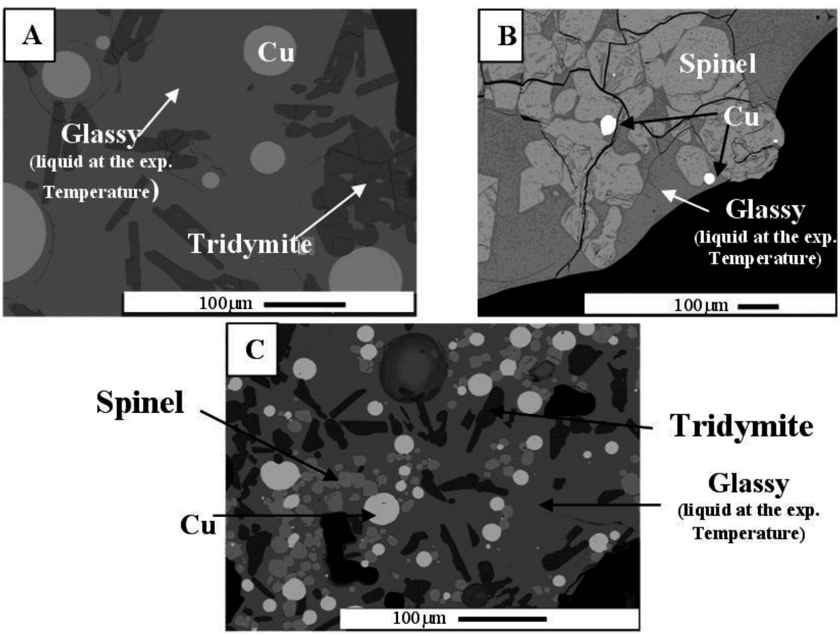

Figure 3: SEM of liquid slag in equilibrium with tridymite or/and spinel at the condition of copper sat. (A:Tridymite sat. 1250°C, B:Spinel sat. 1235°C, C:Tridymite and spinel sat. 1150°C)

With the present experimental technique and careful selection of initial oxide bulk compositions to ensure they are close the anticipated liquidus it was possible to obtain experimental results very close to the target composition.

Phase Equilibrium with Tridymite

Figure 4 shows the relationship between liquidus temperature and Fe/SiO_2 ratio in the tridymite primary phase field. The Fe/SiO_2 ratio increases with a steeply decrement of the liquidus temperature.

The initial mixture of oxides reacted with the silica dish, the reaction being limited to 200 μm in depth. Thus, the un-reacted silica isolated the sample from the platinum wire. However, in one set of experiments, the slag was found to be in contact with the platinum wire. Thus, the slag reached the equililibrium with a Pt-Cu-Fe alloy so that the content of copper in slag was less than that in equilibrium with pure metallic copper. The results of these experiments (see square markers in Figure 4) were used to analyse the effect of copper oxide content in the liquid slag phase on the tridymite liquidus line. As indicated in Figure 4, increasing content of copper in slag, increases the area of stability of liquid slag.

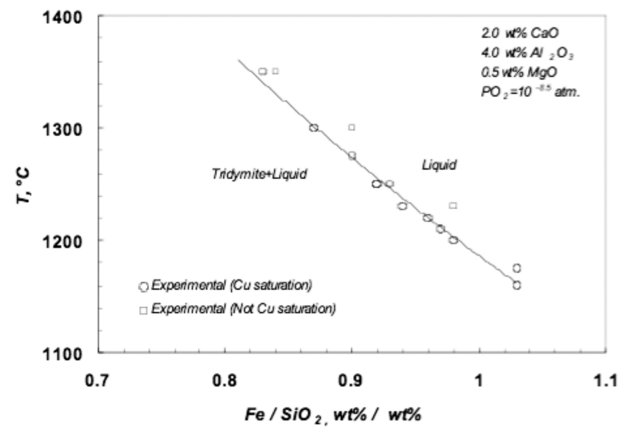

Figure 4: Measured trydimite liquidus line (open marks–Cu sat.; closed marks–Not Cu sat.) for a slag with CaO = 2.0 wt%, MgO = 0.5 wt% and Al_2O_3 = 4.0 wt% at $P_{O2} = 10^{-8.5}$ atm

Phase Equilibrium with Spinel

In contrast to the experiments to determine tridymite liquidus, the liquid composition changes significantly as spinel precipitates; thus, the exact target of MgO, CaO and Al_2O_3 concentrations in the liquidus phase could not be achieved in each experiment. Linear interpolation of the liquidus as a function of Fe/SiO_2 ratio was used to estimate the liquidus values at the exact concentrations of CaO = 2.0 wt%, MgO = 0.5 wt% and Al_2O_3 = 4.0 wt%. The expression which represents the spinel liquidus temperature is given by Equation 1.

$$T[°C]_{liquidus} = 1293.51 - 187.177 / (Fe/SiO_2) + 5.73*(wt\%CaO) + 3.67*(wt\%MgO) + 5.52*(wt\%Al_2O_3) \quad (1)$$

Where the interpolation coefficients for the CaO, MgO and Al_2O_3 concentrations were obtained from the FactSage predictions using thermodynamic databases of the oxide system [6], and the coefficients describing the effect of the Fe/SiO_2 ratio on the spinel liquidus was derived from the present experimental data. Figure 5 illustrates the agreement between experimental results (open circles) and the interpolated values (closed circles). The differences between experimental and interpolated points are in the range of the experimental temperature accuracy of 5°C.

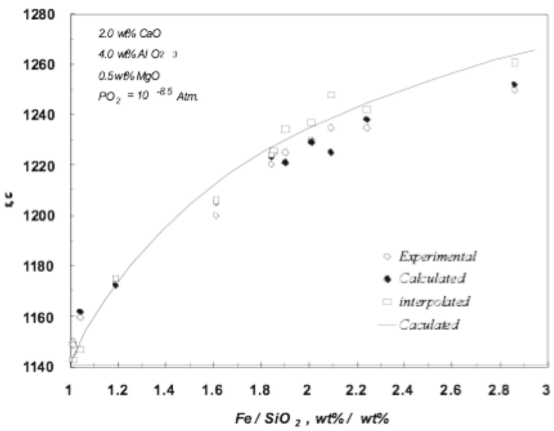

Figure 5: Calculated and experimental spinel liquidus line (open - experimental; closed - interpolated points; circles - variable CaO, MgO and Al_2O_3 concentrations; and square - interpolated points with CaO = 2.0 wt%, MgO = 0.5 wt% and Al_2O_3 = 4.0 wt%) at $PO_2 = 10^{-8.5}$ atm

Circle markers (both open for experimental and closed for interpolated points) present points with variable CaO, MgO and Al_2O_3 concentrations. Square open markers (interpolated) present points with exact concentrations of CaO = 2.0 wt%, MgO = 0.5 wt% and Al_2O_3 = 4.0 wt%.

This figure indicates the accuracy of the interpolation as well as the self-consistency of the experimental dataset.

Experimental and Predicted Phase Diagram

Figure 6 presents the tridymite and spinel liquidus lines. The predictions performed with FactSage using recent thermodynamic databases of oxide system [6] are also included in Figure 6. There is a good agreement between the experimental results and the FactSage predictions [6, 7] for the tridymite liquidus line. However, there is a systematic difference of approximately 10ºC between experimental and predicted liquidus line. In the spinel primary phase field the experimental liquidus temperatures are found to be higher than the predicted values.

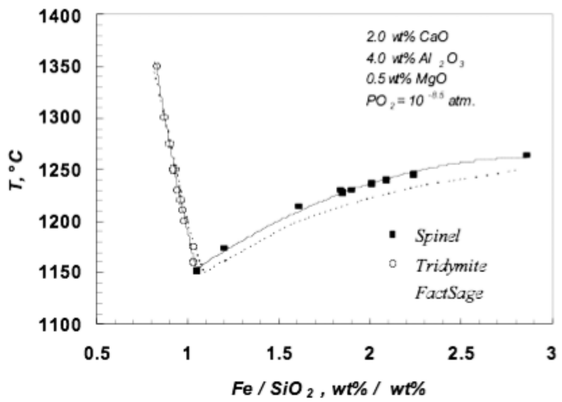

Figure 6: Liquidus trydimite and spinel line for the "Cu_2O-FeO-Fe_2O_3-SiO_2-CaO-MgO-Al_2O_3" slag system in the range of compositions and temperatures directly relevant to electric furnace practice and $PO_2 = 10^{-8.5}$ atm

Content of Dissolved Copper in Slag at Copper Saturation

Figure 7 shows the relationship between temperature and the dissolved copper in slag for the equilibrium between liquid slag and tridymite at metallic copper saturation. Note, that the values of the Fe/SiO_2 ratio and the CaO, MgO, Al_2O_3 concentrations in the slag for all points are different from the exact targeted values; however these differences are not large for the tridymite primary phase field. As a general tendency, the content of copper in slag decreases with increasing temperature. A clear tendency for the content of copper in slag along the spinel liquidus is difficult to obtain due the combined effect of varying temperature, Fe/SiO_2 ratio and CaO, MgO, Al_2O_3 contents in slag.

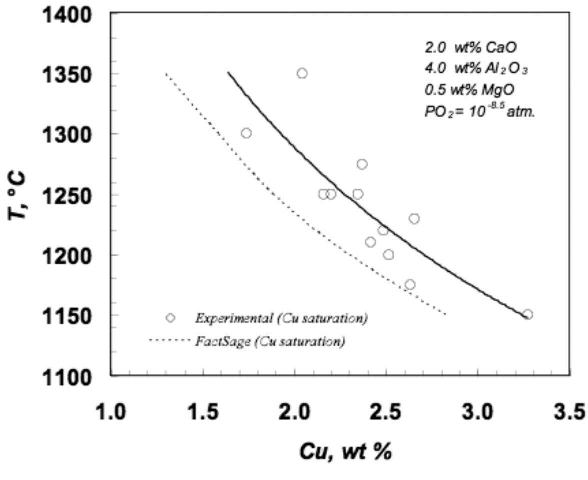

Figure 7: Copper solubility in slag as a function of temperature along the tridymite liquidus at metallic copper saturation for the electric furnace practice (solid line experimental trend) and $PO_2 = 10^{-8.5}$ atm

It is also observed in Figure 7 that the content of copper in slag, at a given temperature, is approximately 0.5 wt% larger than predicted with FactSage [6].

Application of the Results to the Practical Operation

Investigated synthetic slag Cu_2O-FeO_x-SiO_2-Al_2O_3-CaO-MgO system corresponds to the chemical assay of the slag from an electric furnace. Only zinc content (3%) in the form of ZnO was not taken under consideration. The results show the liquidus temperature as a function of Fe/SiO_2 ratio. The spinel or tridymite precipitation is defined for wide temperature range and Fe/SiO_2 ratio, showing comparatively low deviation from existing experimental data for FeO-SiO_2 system. The results are used in the interpretation of phenomena in the electric furnace combined with CFD and heat transfer modelling, such as precipitation of magnetite at the slag/copper matte interface and slag/refractory interface.

The important aspect of obtained results is determined Cu_2O content in the phases formed in the fast quenched slag for determined temperature and oxygen potential. The high cuprous oxide content points out the very important question of the limit of Cu_2O reduction. However, the system was equilibrated with metallic copper and the slag in the electric furnace is equilibrated with copper matte.

CONCLUSIONS

The experimental phase diagram of Cu_2O-FeO-Fe_2O_3-SiO_2-CaO-MgO-Al_2O_3 system at the oxygen partial pressure of $10^{-8.5}$ atm in the range of compositions and temperatures directly relevant to the slag cleaning electric furnace was constructed. The target slag composition was 2 wt% of CaO, 0.5 wt% of MgO and 4.0 wt% of Al_2O_3 and the experimental temperature range was between 1150 and 1350ºC. Spinel and tridymite liquidus for the system were constructed.

The spinel liquidus temperatures were described as a function of the Fe/SiO_2 ratio and the CaO, MgO and Al_2O_3 concentrations.

The obtained phase diagram can be used as a guide for the copper slag cleaning electric furnace operation to define temperatures and slag compositions where the slag is liquid for the limits of tridymite and spinel start to precipitate.

The experimental results were compared with the FactSage predictions. In general, there is good agreement between the predictions and the experimental results; however, further optimization of FactSage database can further improve accuracy of predictions.

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