Microanalysis and Experimental Techniques for the Determination of Multicomponent Phase Equilibria for Non-ferrous Smelting and Recycling Systems

Taufiq Hidayat, Peter C. Hayes and Evgueni Jak

Abstract Accurate description of complex phase equilibria provide the foundations for the improvement of non-ferrous pyrometallurgical smelting and recycling processes. Recent advances in microanalysis and experimental techniques enable accurate phase equilibria characterisation. Quantitative microanalytical techniques including Electron Probe X-ray Microanalysis and Laser Ablation ICP-MS enable the concentrations of major and minor elements present in different phases in samples to be accurately measured providing data that cannot be obtained using bulk chemical analysis techniques. High-temperature equilibration experiments coupled with the subsequent analysis of elementary reactions at micro- and macro-scales ensure the attainment of equilibrium conditions, and therefore, ensure true phase equilibria information is obtained. Examples of the application of the improved methodology on the investigation of phase equilibria of low-order and complex, multi-component gas/slag/matte/metal/solids Cu_2O–PbO–ZnO–Al_2O_3–CaO–MgO–FeO–Fe_2O_3–SiO_2–S systems and the distribution of minor element are provided. The experimental study is closely integrated with thermodynamic database development for the above system. Example of implementation of the research outcomes into industrial operations is demonstrated.

Keywords Pyrometallurgy · Non-ferrous metals · Microanalysis
Phase equilibria · Minor element distribution

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Introduction

Whilst the bulk chemical analysis of the phases present in non-ferrous pyrometallurgical smelting and recycling processes is routinely undertaken to monitor and control these processes, further important information can be obtained from the detailed examination of these industrial samples. Microanalysis of the materials provides insights that can be combined with knowledge of phase equilibria and thermodynamic and used as a guide to further process improvement and optimisation.

The latest developments of micro-analytical and high-temperature equilibration techniques, which incorporate careful analysis of elementary reaction processes, enable the complete characterization of complex multi-phase systems. Information previously difficult to obtain can now be determined precisely and accurately. An overview of recent progress on the use of microanalysis techniques, their incorporation into experimental methodologies and examples of their application for the determination of phase equilibria for non-ferrous pyrometallurgical smelting and recycling processes, are given in the present article.

Development of Microanalysis Techniques

Microanalysis provides the ability to directly and accurately measure phase compositions at high spatial resolutions, to identify the presence of second phases in samples and to determine changes in local compositions within phases. These important characteristics and capabilities can be used to examine and measure phases that are present in solid or liquid states at the reaction temperatures in samples obtained from industrial operations or from laboratory studies.

Scanning Electron Microscope and Energy-Dispersive X-Ray Spectroscopy

Scanning electron microscope (SEM) is a powerful tool for capturing high-resolution images revealing the topography of free surfaces and providing qualitative compositional profiles of a sample. The SEM can be equipped with an Energy-Dispersive X-ray Spectroscopy (EDS) detector, which enables semi-quantitative analysis of the elements in the sample. The SEM can reach very high magnification to nanoscale resolution. Figure 1 shows example of SEM image with back-scattered electron mode and EDS analysis of a slag sample containing matte inclusions. It can be seen in this example that high spatial resolution of the SEM provides qualitative identification of elements in a sub-micron matte particle embedded in the slag phase.

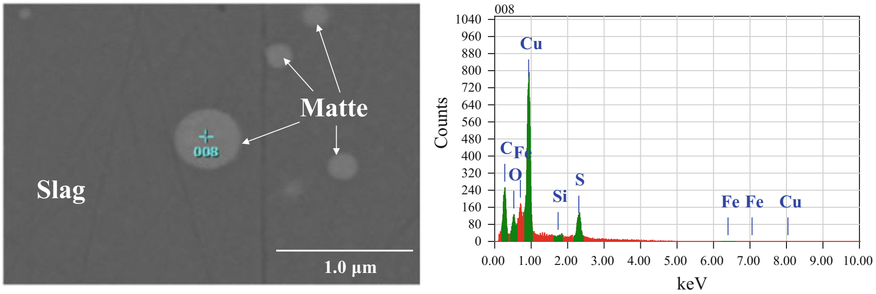


Fig. 1 SEM back-scattered electron (BSE) image and EDS analysis result of a slag sample

Electron Probe Micro-Analysis

The Electron Probe Micro-Analyser (EPMA) with Wavelength Dispersive Detectors (WDD) provides direct measurement of elemental concentrations from solid samples at spatial resolutions as low as 1-µm level. EPMA uses characteristic X-rays excited by the sample after it is bombarded with electrons in a focussed beam to identify and quantify elements present in the sample. EPMA demonstrates good analysis precision of between 0.3 and 0.8% for the measurements of major elements [1]. The selection of appropriate standards and the use of fundamentally-based atomic number, absorption and fluorescence (ZAF) correction procedures enables accurate analyses to be undertaken without destroying the samples. Additional software, i.e. Probe for EPMA software [2], can be added into the system to improve acquisition, automation and analysis of the EPMA data.

The EPMA used in a point analysis mode can be used to accurately measure the compositions of phases as small as 5 µm diameter, depending on the elements present and their relative concentrations. By undertaking a series of point analyses, composition profiles within phases can be determined. Some limitations of the EPMA technique include its inability to measure low atomic number elements (such as lithium) and detection limit (which is restricted to <100 ppm). The EPMA detection of an element is related to its ability to distinguish the X-ray peak intensity of the element and the surrounding off-peak intensity (background). Small inaccuracies in the background position can introduce large errors in the EPMA analysis of trace elements [3]. Careful background characterization and the use of a multi-point regression technique to determine the background curvature provides improvement of EPMA precision and accuracy for trace element analysis. This approach is available in “Multi-Point Background” feature of the EPMA software [2].

Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Trace and ultra-trace element concentrations in solid samples with the smallest area of 20 μm can be measured using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The micro-analytical system consists of a laser-ablation chamber and ICP-MS detection system [4]. A small mass of sample is removed from selected area of solid sample (destructive method) by the laser through desorption and thermal evaporation into an aerosol of small particles. These particles are transported by a flow of gas to the ICP torch for ionization and the resulting ions are then detected and counted by the mass spectrometry. The micro-analysis technique has minimum detection limits between 10 ppb and 1 ppm depending on the elements being measured and the matrix material. The lowest analysis precision and accuracy are 3% and 9%, respectively, when tested on certified oxide glass standard [1].

By using EPMA in conjunction with LA-ICP-MS the composition of all phases, and major and minor elements can be determined. This greatly extends the range of capabilities of these microanalysis techniques and provides further opportunities for detailed characterisation and interpretation of the information available in these metallurgical samples.

Key Information Provided by Microanalysis

The high-resolution imaging, qualitative and quantitative compositional analysis capabilities obtained from the combined microanalysis techniques provide the key information required to understand physical and chemical behaviour in metallurgical systems. The combined-microanalysis techniques with expert analysis can be used to determine whether solid phases are dissolving or and precipitating from solutions, diffusion rates based on compositional profile in quenched liquid or solid phases, and other elementary reactions.

An example of the interpretation of microanalysis result is provided in Fig. 2 [5]. Two samples from experiments at gas/matte/spinel equilibria in the Cu–Fe–O–S system at 1473 K (1200 °C) under $CO/CO_2/SO_2/Ar$ atmosphere were analyzed using SEM, one with initial mixture having low Cu in matte (Fig. 2a) and another with initial mixture having high Cu in matte (Fig. 2b). Figure 2a shows the precipitation of a solid spinel according to reaction (1) during compositional movement from low to high Cu in matte. Figure 2b shows the irregular shape of the spinel solid on the matte/substrate interface indicating the dissolution of Fe_3O_4 into FeS matte according to reaction (2) during compositional movement from high to low Cu in matte.

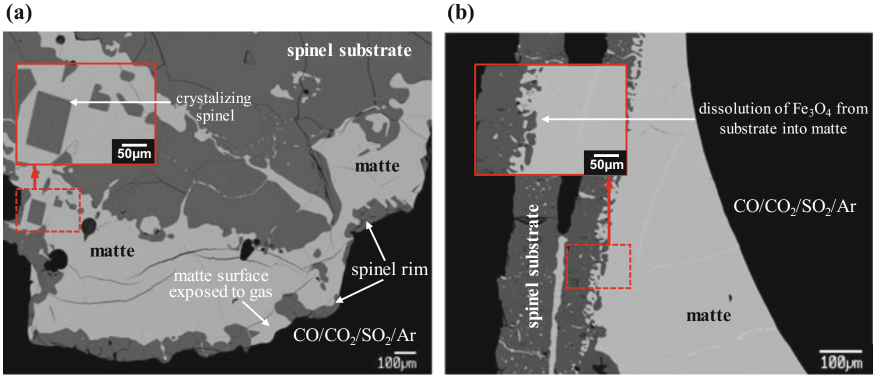


Fig. 2 SEM BSE images of microstructures from gas/matte/spinel equilibria in the Cu–Fe–O–S system at T = 1200 °C, $P(SO_2) = 0.25$ atm, and $P(O_2) = 10^{-8.3}$ atm: **a** Approaching from low to high Cu in matte (61.1wt% Cu to 71.9wt% Cu), equilibration time = 24 h; and **b** Approaching from high to low Cu in matte (79.9wt% Cu to 71.9wt% Cu), equilibration time = 3 h [5]

$$3FeS\ (matte) + 10CO_2\ (gas) \rightarrow Fe_3O_4\ (spinel) + 10CO\ (gas) + 3SO_2\ (gas) \quad (1)$$

$$Fe_3O_4\ (spinel) + 10CO\ (gas) + 3SO_2\ (gas) \rightarrow 3FeS\ (matte) + 10CO_2\ (gas) \quad (2)$$

Further in-depth analysis and interpretation of the elementary reactions will provide useful information for understanding complex phenomena found in the industrial metallurgical processes, such as the mechanism of formation/origin of phases, precious metals loss, degradation of furnace lining, etc.

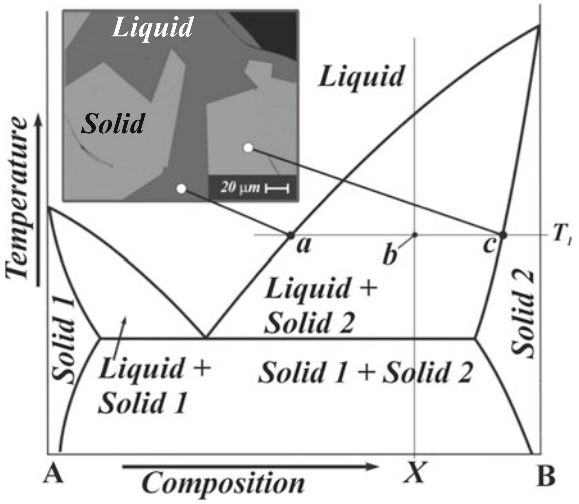
High-Temperature Equilibration Techniques

General Description of the Technique

The general approach to high-temperature equilibration involving equilibration/quenching/microanalysis, used in the characterisation of metallurgical systems, has been previously described [6, 7] but is being continuously improved thereby extending the range of chemical compositions and process conditions that can be characterised.

Figure 3 [8] is provided as reference for a brief explanation of the technique. The experiment starts by preparing mixtures of solids from the analytically pure powders, pre-sintered solids or pre-melted master slags/mattes to obtain after equilibration a predetermined bulk composition X with two or more phases present in equilibrium. Each mixture is pelletised and placed on a specimen holder and suspended on a wire in the uniform temperature hot-zone of a vertical electrically-heated furnace. The temperature is controlled to achieve overall

Fig. 3 Schematic phase diagram showing the initial bulk composition (X) at temperature T_1 selected for phase diagram solidus and liquidus determination [8]



accuracy within 5 K or better. The gas atmosphere for “open-system experiments” is maintained by passing over the samples mixtures of pure gases, such as, CO, CO_2, H_2, Ar, SO_2, etc. The proportions of gases are determined following thermodynamic calculations using the FactSage software package [9] and are controlled using U-tube pressure differential type flow-meters. The resulting $P(O_2)$ for the SO_2-free containing atmosphere is confirmed using DS-type oxygen probe (supplied by Australian Oxygen Fabricators, AOF, Melbourne, Australia).

After equilibration, the samples are rapidly quenched into cold water, iced water or salt solution so that the liquid phases are converted to glass or fine microcrystalline material, and the solid crystals that exist at the equilibration temperature are frozen unchanged. The final microstructure, phases and their compositions represent the equilibrium phase assemblage existing at the selected process conditions (see example of final microstructure in Fig. 3).

The equilibrated samples are mounted in epoxy resin, polished using automatic TegraPol-31 polisher (Struers, Denmark) and carbon coated using QT150TES carbon coater (Quorum Technologies, UK). Initial examination of the microstructure of the samples are carried out using conventional metallurgical optical microscopy and SEM. The compositions of the phases (glass, microcrystalline and solids) are then measured using combined-microanalysis techniques. EPMA JEOL JXA 8200L (trademark of Japan Electron Optics Ltd., Tokyo) is used for major elements analysis, and LA-ICP-MS, which consists of an NWR193 Laser Ablation System (Electro Scientific Industries Inc, Portland, USA) and an Agilent 8800 ICP-MS (Agilent Technologies, Santa Clara, USA) is used for minor elements analysis.

Further Development of the Technique

The high-temperature equilibration technique is continuously being improved. Phase equilibrium determination experiments can now be undertaken with a range of specimen holder materials; ceramic crucibles, in thin metal foils or on a substrate made of a primary phase solid. The geometric arrangement of the samples has also been modified. The original technique involved placing the liquid inside the container. Now particularly for liquidus determination experiments, the sample is attached by surface tension to the outside of artificial primary phase substrate support materials. This approach results in thin (50–200 μm) films of multi-phase slag/metal/matte/speiss/solid material. The thin film enables rapid equilibration with the gas phase to be obtained and greatly increased rates of quenching of the samples following equilibration to be achieved. These improvements have greatly increased the range and combinations of process conditions that can be studied, for example, temperatures, oxygen and sulphur partial pressures [5, 10–13].

"Closed-system experiments" are undertaken to determine phase equilibria by using sealed quartz ampoules. The sample mixtures are pelletised before inserting into closed end silica tubes. The tubes are sealed under vacuum using an oxy-fuel torch. This approach is suitable for condensed phase equilibration, for example equilibration between slag/matte/metal/tridymite phases [14]. Following equilibration at temperature the ampoules containing the samples are quenched and the resulting phase assemblage is characterised using the microanalyical techniques described above. This technique is for the characterisation of systems containing species that have high vapour pressures.

One of the most recent improvements is the application of the four-point test approach. The approach is used to ensure the achievement of equilibrium through various tests and analyses which include: (1) test of equilibration time; (2) analysis of phase homogeneity; (3) test of directions of approach towards the final equilibrium point; and (4) systematic analysis of reactions specific to the system. Systematic analysis of reactions for new investigated system is essential in phase equilibria studies to ensure appropriate experimental methodology specific to the system is developed and used [5, 12]. This step will ensure the achievement of equilibrium condition and the attainment of reliable experimental results.

A recent phase equilibria study in the ZnO–containing systems at intermediate $P(O_2)$ demonstrated the need for critical analysis of elementary reactions, reaction mechanisms and pathways during equilibration to identify potential sources of uncertainties before systematic measurements of a system. Figure 4 shows significant discrepancies between recent data reported by the authors [15] and previous study [16] for the ZnO–"FeO"–SiO_2 system at 1250 °C and $P(O_2) = 10^{-8}$ atm. The uncertainties in the results appear to be the result of uncontrolled Zn(g) vaporisation in previous studies by these authors [16–20], which affects the effective oxygen activity of the slag through the following reaction:

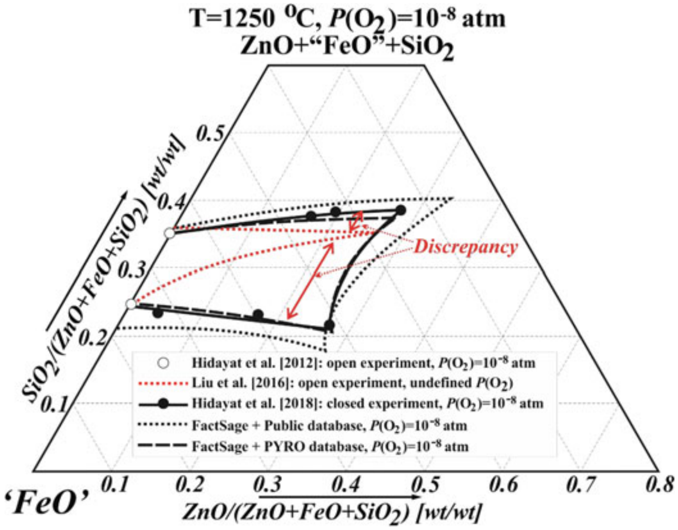


Fig. 4 Liquidus isotherms for the ZnO–"FeO"–SiO_2 system at T = 1250°C (1523 K) and $P(O_2) = 10^{-8}$ atm, calculated with FactSage using Public [22] and PYROSEARCH [21] databases, and experimentally determined by the authors [15] and Liu et al. [16]

$$\text{ZnO (slag)} + \text{CO (gas)} = \text{Zn (gas)} + \text{CO}_2 \text{ (gas)} \tag{3}$$

and

$$2\,\text{FeO (slag)} + \text{ZnO (slag)} = \text{Fe}_2\text{O}_3 \text{ (slag)} + \text{Zn (gas)} \tag{4}$$

Reaction (3) acts as an effective buffer at the slag surface restricting the bulk slag from the reaction with the CO/CO_2 gas, and reaction (4) may be viewed as an effective "pump" of the oxygen left by ZnO during Zn (gas) vaporisation into the bulk slag:

$$\text{ZnO (slag)} = \text{Zn (gas)} + \text{O (slag)} \tag{5}$$

and

$$2\,\text{FeO (slag)} + \text{O (slag)} = \text{Fe}_2\text{O}_3\text{(slag)} \tag{6}$$

Reaction (4) is a combination of reactions (5) and (6) which can be expressed simply by the following statement: as zinc vaporises from the slag the effective oxygen partial pressure of the slag phase is increased. This effect is more significant at higher ZnO concentrations. The increasing discrepancies at higher ZnO concentration in the slag is consistent with this reaction mechanism. In summary, the liquidus data reported in previous studies by the research group [16–20] do not correspond to the reported oxygen pressures and the effective oxygen activities in the slags in those experiments are unknown.

The experimental study by the authors [15] on phase equilibria in the ZnO–“FeO”–SiO_2–“Cu_2O” system in equilibrium with liquid copper at 1250 °C at low copper oxide concentrations in slag was initiated and undertaken to resolve these discrepancies. High temperature equilibration–rapid quenching–EPMA technique combined with a primary phase substrate support and closed system approach with Cu metal introduced to determine effective equilibrium oxygen partial pressure from the Cu_{metal}/Cu_2O_{slag} equilibria has been applied to provide accurate information on liquidus and corresponding solid compositions in different primary phase fields. The ZnO-containing “Cu_2O”-free liquidus at $P(O_2) = 10^{-8}$ atm was constructed by extrapolation of the experimental points from the ZnO–“FeO”–SiO_2–“Cu_2O” system (shown in Fig. 4) using calibrations determined by FactSage predictions with the current thermodynamic database (PYROSEARCH database) [21]. The calibration increments were less than 5 wt% and the final uncertainty of the experimental liquidus compositions was evaluated to be less than 1 wt%. The closed system approach used in this study has considerable potential for extending the range of chemical systems with relatively high vapour of metal species.

Application of the Techniques for the Phase Equilibria Studies

The application of the improved high-temperature equilibration and the advanced micro-analysis techniques can be demonstrated with reference to the current program undertaken at the Pyrometallurgy Innovation Centre (PYROSEARCH) at the University of Queensland and supported by the consortia of leading international metallurgical companies. These high temperature studies on copper-lead-zinc-containing systems involve gas/slag/matte/metal/speiss/solids oxide and sulphide systems with major elements “Cu_2O”–PbO–ZnO–FeO–Fe_2O_3–SiO_2–S with the addition of slagging elements Al_2O_3, CaO, MgO and selected minor elements, including As, Sn, Sb, Bi, Ag, Au. The research program provides not only experimental data, but also sophisticated thermodynamic databases and predictive modelling tools [23, 24] necessary to achieve the improvements of pyrometallurgical processes.

Phase Equilibria Study in the Copper-Containing System

The combined high-temperature equilibration and micro-analysis techniques have been applied in the investigation of the copper-containing system. Figure 5 shows recent experimental data [5, 13, 25] on the gas/matte/spinel and gas/slag/matte/spinel

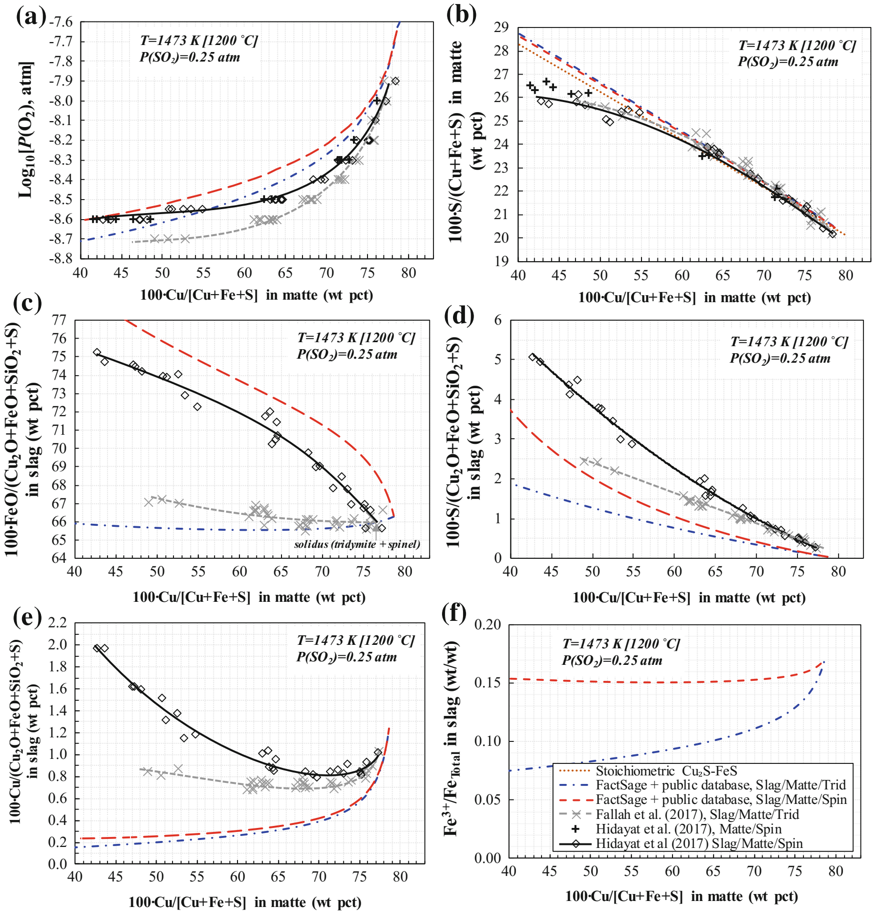


Fig. 5 The gas/slag/matte/spinel (or tridymite) equilibria in the Cu–Fe–O–S–Si system at T = 1200 °C and $P(SO_2)$ = 0.25 atm: **a** Oxygen partial pressure ($P(O_2)$, atm) versus Cu in matte; **b** Concentration of sulphur in matte versus Cu in matte; **c** FeO in slag versus Cu in matte; **d** Concentration of sulphur in slag versus Cu in matte; **e** Concentration of copper in slag versus Cu in matte; and **f** Ferric iron to total iron ratio in slag versus Cu in matte. Experimental data are from [5, 13, 25]. Dashed lines are FactSage predictions using the public database [22]

(or tridymite) equilibria in the Cu–Fe–O–S–Si system at T = 1200 °C and $P(SO_2)$ = 0.25 atm covering wide range Cu in matte. The experimental data can be used for the evaluation of effects of oxidation condition and fluxing on the slag liquidus, percent solid and chemical copper loss in the slag.

Phase Equilibria Study in the Lead-Containing System

An example of the application of the integrated high-temperature equilibration and micro-analysis techniques for the lead-containing system is provided in Fig. 6. New experimental data have been obtained for the slag/matte/metal/tridymite equilibria in the Pb–Cu–Fe–O–S–Si system at T = 1200 °C for fixed Cu/[Cu + Pb] ratios in matte covering wide range Pb in slag. In copper industry, the converting of mattes with high lead content creates a considerable technical difficulties. The lead smelting and refining systems also produce mixed lead-copper containing phases. The experiments involving slag/matte/metal/tridymite equilibria provide important data on the tridymite liquidus of the complex slag as well as on the partitioning of Pb, Cu, Fe and S between phases.

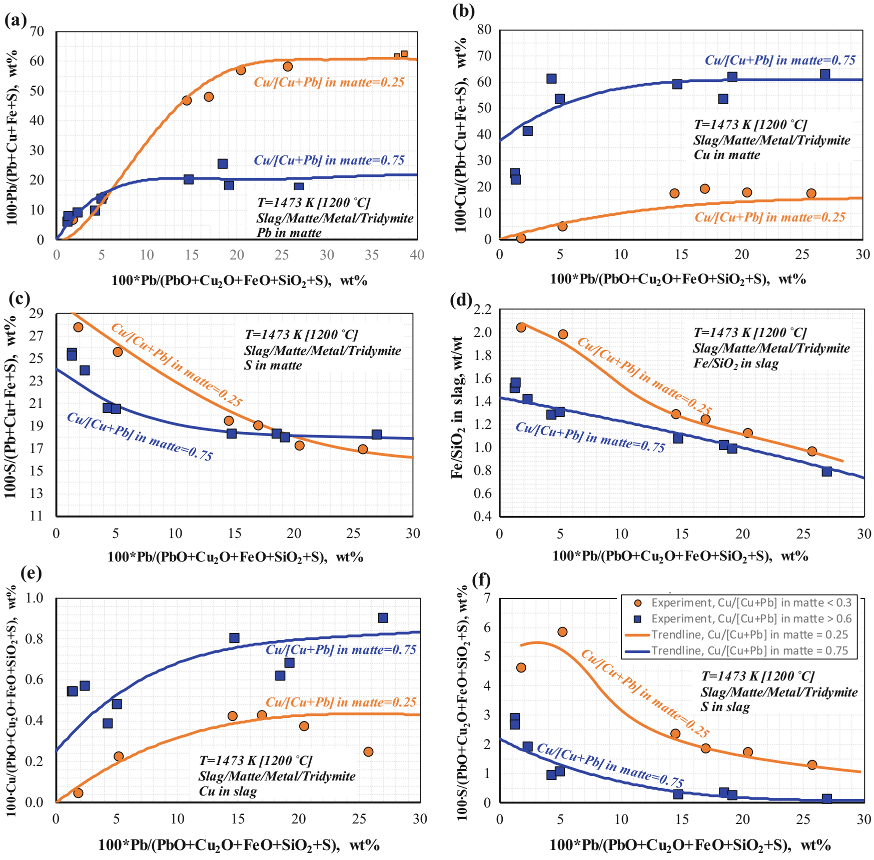


Fig. 6 The slag/matte/metal/tridymite equilibria in the Pb–Cu–Fe–O–S–Si system at T = 1200 °C for fixed Cu/[Cu + Pb] ratios in matte: **a** Concentration of Pb in matte versus Pb in slag; **b** Concentration of Cu in matte versus Pb in slag; **c** Concentration of S in matte versus Pb in slag; **d** Fe/SiO$_2$ in slag versus Pb in slag; **e** Concentration of Cu in slag versus Pb in slag; and **f** Concentration of S in slag versus Pb in slag

Distribution of Minor Element Between Phases

The application of the present approach for the determination of distribution of minor elements between phases has been demonstrated in previous studies [10, 11]. The distribution coefficient of Ag in gas/slag/matte/solid equilibria in the Cu–Fe–O–S–Si system at T = 1200 °C and $P(SO_2)$ = 0.25 atm is provided in Fig. 7.

In the studies [10, 11], the LA-ICP-MS was used to accurately measure the Ag concentrations in the slags at very low concentrations in the range of 2–21 ppm. The experimental work on the minor element distributions for the gas/slag/matte/solid equilibria is still ongoing, and has been extended to include As–Bi–Sb–Sn–Ag–Au in the gas/slag/matte/metal/speiss/solids equilibria of the complex Cu_2O–PbO–ZnO–Al_2O_3–CaO–MgO–FeO–Fe_2O_3–SiO_2–S system.

Industrial Application of Phase Equilibria Data

An example of industrial application of phase equilibria data in the copper smelting is provided in Fig. 8. The figure shows fluxing diagram at constant T = 1200 °C and $P(SO_2)$ = 0.25 atm at variable Cu in matte, Al_2O_3 in slag and CaO in slag. The experimental data without and with Al_2O_3+CaO in slag are from previous [13, 25] and recent studies by the authors. Industrial data taken from literature [28] are plotted in the figure. The fluxing diagram gives indication of the effects of matte grade and slag composition on the phase assemblage and phase proportion. The presence of additional components, such as MgO from raw materials, or Cr_2O_3 from refractory materials will further influence the shape of this fluxing diagram.

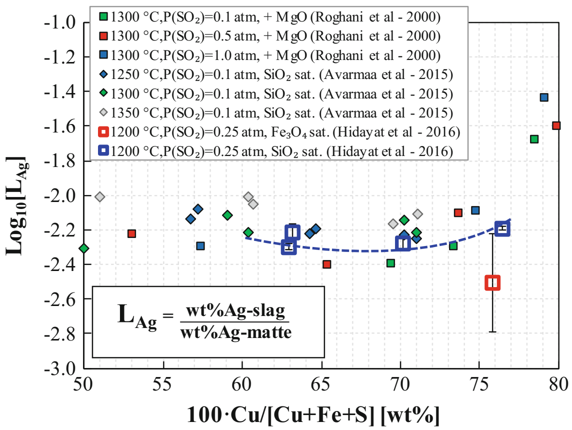


Fig. 7 Distribution coefficient of Ag between slag and matte as a function of matte grade for the gas/slag/matte/solid equilibria in the Cu–Fe–O–S–Si system at T = 1200 °C and $P(SO_2)$ = 0.25 atm. Previous data are from [10, 11, 26, 27]

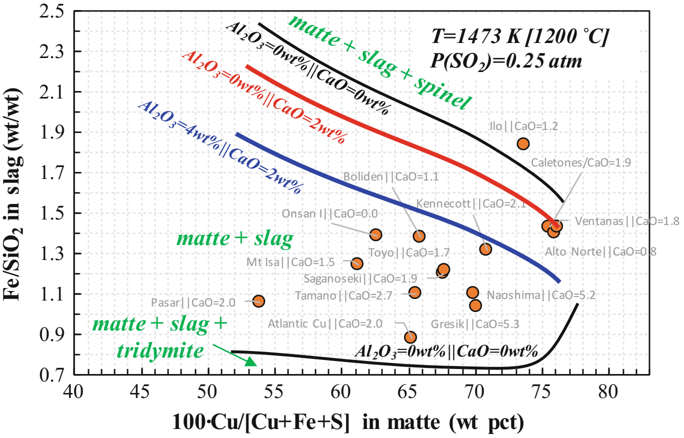


Fig. 8 Fluxing diagram in the Cu–Fe–O–S–Si–Al–Ca system at T = 1200 °C and $P(SO_2)$ = 0.25 atm showing Fe/SiO_2 ratio in slag as a function of Cu in matte at different Al_2O_3 and CaO concentrations in slag. Experimental lines without and with Al_2O_3+CaO in slag are taken from previous [13, 25] and recent studies by the authors. Industrial data are taken from literature [28]

Conclusions

Coupled high-temperature equilibration and microanalysis techniques can now be used to characterize complex phase equilibria in non-ferrous pyrometallurgical processes. The improved methodology has been successfully applied for the investigation of phase equilibria in a wide range of systems, from low-order to complex, multi-component gas/slag/matte/metal/solids Cu_2O–PbO–ZnO–Al_2O_3–CaO–MgO–FeO–Fe_2O_3–SiO_2–S system and distribution of minor element between phases. The development of these improved microanalytical techniques and laboratory-based procedures has further extended the range of phase combinations, compositions and process conditions for which accurate phase equilibium information can be obtained. The use of these microanalyical techniques coupled with these fundamental studies also enables the process conditions present in high temperature industrial reaction systems to be characterised. This work is part of larger research program that provides experimental data, as well as state-of-the art thermodynamic databases and predictive modelling tools supported by consortia of leading international metallurgical companies.

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References

1. Chen J, Allen CM, Azekenov T, Ushkov LA, Hayes P, Jak E (2016) Quantitative determination of trace/ultra trace elements concentration in slag and matte generated in copper smelting using microanalysis techniques. In: 9th international copper conference, The Mining and Materials Processing Institute of Japan, Japan Mining Industry Association, Kobe, Japan, paper no PY18-1
2. Donovan J, Kremser D, Fournelle J (2012) Probe for EPMA: acquisition, automation and analysis. Probe Software, Inc., Eugene, Oregon
3. Jercinovic MJ, Williams ML, Allaz J, Donovan JJ (2012) Trace analysis in EPMA. IOP Conf Ser Mater Sci Eng 32
4. Mokgalaka NS, Gardea-Torresdey JL (2006) Laser ablation inductively coupled plasma mass spectrometry: principles and applications. Appl Spectrosc Rev 41:131–150
5. Hidayat T, Hayes P, Jak E (2018) Experimental investigation of gas/matte/spinel equilibria in the Cu-Fe-O-S system at 1473 K (1200 °C) and P(SO2) = 0.25 atm. J Phase Equilib Diffus 39:138–151
6. Jak E, Hayes PC, Lee H-G (1995) Improved methodologies for the determination of high temperature phase equilibria. Met Mater (Seoul) 1(1):1–8
7. Jak E (2012) Integrated experimental and thermodynamic modelling research methodology for metallurgical slags with examples in the copper production field. In: 9th international conference molten slags, fluxes and salts, The Chinese Society for Metals, Beijing, China, paper no W077
8. Hidayat T, Hayes PC, Jak E (2012) Experimental study of ferrous calcium silicate slags: phase equilibria at between 10^{-5} atm and 10^{-7} atm. Metall Mater Trans B 43(1):14–26
9. FactSage 7.0 (2015) FactSage thermochemical software. http://www.factsage.com/
10. Hidayat T, Fallah Mehrjardi A, Hayes P, Jak E (2016) Experimental study of slag/matte/spinel equilibria and minor elements partitioning in the Cu-Fe-O-S-Si system. In: 10th international conference molten slags, fluxes and salts, The Minerals, Metals and Materials Society, Seattle, USA
11. Hidayat T, Fallah Mehrjardi A, Hayes P, Jak E (2016) Experimental study of metal-slag and matte-slag equilibria in controlled gas atmospheres. In: 9th international copper conference, The Mining and Materials Processing Institute of Japan and Japan Mining Industry Association, Kobe, Japan, paper no PY22-3
12. Fallah-Mehrjardi A, Hidayat T, Hayes PC, Jak E (2017) Experimental investigation of gas/slag/matte/tridymite equilibria in the Cu-Fe-O-S-Si system in controlled gas atmospheres: development of technique. Metall Mater Trans B 48(6):3002–3016
13. Fallah-Mehrjardi A, Hidayat T, Hayes PC, Jak E (2017) Experimental investigation of gas/slag/matte/tridymite equilibria in the Cu-Fe-O-S-Si system in controlled gas atmospheres: experimental results at 1473 K (1200 °C) and P(SO2) = 0.25 atm. Metall Mater Trans B 48(6):3017–3026
14. Chen J, Allen C, Hayes P, Jak E (2016) Experimental study of slag/matte/metal/tridymite four phase equilibria and minor elements distribution in “Cu-Fe-Si-S-O” system by quantitative microanalysis techniques. In: 10th international conference molten slags, fluxes and salts, The Minerals, Metals and Materials Society, Seattle, USA
15. Hidayat T, Hayes P, Jak E (2018) Phase equilibria in the ZnO-“FeO”-SiO_2 system in reducing atmosphere and in the ZnO–“FeO”–SiO_2–“Cu_2O” system in equilibrium with liquid copper metal at 1250 °C (1523 K). Metall Matter Trans B (In press)

16. Liu H, Cui Z, Chen M, Zhao B (2016) Phase equilibrium study of ZnO-”FeO”-SiO_2 system at fixed Po_2 10^{-8} atm. Metall Mater Trans B 47(1):164–173
17. Liu H, Cui Z, Chen M, Zhao B (2014) Phase equilibrium study of ZnO-”FeO”-SiO_2 system at fixed $Po_2 = 10^{-8}$ atm. In: 6th annual high temperature processing symposium, Swinburne University of Technology, Hawthorn, Australia
18. Liu H (2016) Phase equilibria studies of zinc-containing copper smelting slags. The University of Queensland, Brisbane, Australia
19. Liu H, Cui Z, Chen M, Zhao B (2016) Phase equilibria studies of ZnO-containing slags at copper smelting conditions. In: 9th international copper conference, The Mining and Materials Processing Institute of Japan and Japan Mining Industry Association, Kobe, Japan, paper no PY22-1
20. Liu H, Cui Z, Chen M, Zhao B (2016) Phase equilibria study of the ZnO-”FeO”-SiO_2-Al_2O_3 system at Po_2 10^{-8} atm. Metall Mater Trans B 47(2):1113–1123
21. Pyrometallurgy Innovation Centre (2015) PYROSEARCH databases for FactSage thermochemical software. The University of Queensland, Brisbane, Australia
22. FactSage 7.0 (2015) FToxid and FTmisc databases. http://www.factsage.com/
23. Shevchenko M, Hayes PC, Jak E (2018) Development of a thermodynamic database for the multicomponent PbO-“Cu_2O”-FeO-Fe_2O_3-ZnO-CaO-SiO_2 system for pyrometallurgical smelting and recycling. In: Peter hayes symposium on pyrometallurgy, The Metallurgy and Materials Society of the Canadian Institute of Mining, Metallurgy and Petroleum, The Society for Mining, Metallurgy and Exploration, and The Minerals, Metals and Materials Society, Ottawa, Canada
24. Shishin D, Hayes PC, Jak E (2018), Multicomponent thermodynamic databases for complex non-ferrous pyrometallurgical processes. In: Peter Hayes symposium on pyrometallurgy, The Metallurgy and Materials Society of the Canadian Institute of Mining, Metallurgy and Petroleum, The Society for Mining, Metallurgy and Exploration, and The Minerals, Metals and Materials Society, Ottawa, Canada
25. Hidayat T, Fallah Mehrjardi A, Hayes P, Jak E (2018) Experimental investigation of gas/slag/matte/spinel equilibria in the Cu-Fe-O-S-Si system at 1473 K (1200 °C) and $P(SO_2) = 0.25$ atm. Metall Matter Trans B. https://doi.org/10.1007/s11663-018-1262-3
26. Roghani G, Takeda Y, Itagaki K (2000) Phase equilibrium and minor element distribution between FeO_x-SiO_2-MgO-based slag and Cu_2S-FeS matte at 1573 K under high partial pressures of SO_2. Metall Mater Trans B 31B(4):705–712
27. Avarmaa K, O’Brien H, Johto H, Taskinen P (2015) Equilibrium distribution of precious metals between slag and copper matte at 1250–1350 °C. J Sustain Metall 1216–228
28. Ramachandran V, Diaz C, Eltringham GA, Jiang CY, Lehner T, Mackey PJ, Newman CJ, Tarasov A (2003) Primary copper production-a survey of operating world copper smelters. Paper presented at the Copper 2003-Cobre 2003, Santiago, Chile