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INTEGRATED EXPERIMENTAL AND MODELLING RESEARCH FOR NON-FERROUS SMELTING AND RECYCLING SYSTEMS

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Abstract

The chemistries of industrial pyrometallurgical non-ferrous smelting and recycling processes are becoming increasingly complex. Optimisation of process conditions, charge composition, temperature, oxygen partial pressure, and partitioning of minor elements between phases and different process streams require accurate description of phase equilibria and thermodynamics which are the focus of the present research. The experiments involve high temperature equilibration in controlled gas atmospheres, rapid quenching and direct measurement of equilibrium phase compositions with quantitative microanalytical techniques including electron probe X-ray microanalysis and Laser Ablation ICP-MS. The thermodynamic modelling is undertaken using computer package FactSage with the quasi-chemical model for the liquid slag phase and other advanced models. Experimental and modelling studies are combined into an integrated research program focused on the major elements Cu-Pb-Fe-O-Si-S system, slagging Al, Ca, Mg and other minor elements. The ongoing development of the research methodologies has resulted in significant advances in research capabilities. Examples of applications are given.

Keywords: copper and lead smelting, recycling, slag, phase equilibria, thermodynamic modelling, liquidus, minor elements distribution.

1. Introduction

Economic and environmental issues require optimisation of the metallurgical primary and recycling operations that in turn needs accurate and reliable information on high temperature chemistry of increasingly complex slag/matte/metal systems. The lack of data and reliable models exists due to difficulties in high temperature experiments and thermodynamic modelling. Recent advances in analytical techniques, experimental methodologies, computer power and thermodynamic modelling theory provide new opportunities in this field. Present paper i) outlines recent progress by the authors and ii) gives examples of the integrated experimental and thermodynamic modelling research on the high temperature slag/matte/metal system with major elements Cu-Pb-Fe-O-Si-S, slagging elements Al, Ca, Mg and other minor elements such as As, Ag, Au, Sb, Sn, Bi and Zn. This research program is undertaken to support smelting and recycling production of copper, lead and other non-ferrous metals.

2. Research Tools

2.1. Experimental Methodology

The equilibration/quenching/EPMA experimental approach that is being continuously developed and applied to the increasingly complex systems is briefly explained with reference to Figure 1 [1]. An artificial oxide mixture prepared from the analytically pure powders, pre-sintered solids or pre-melted master slags to obtain after equilibration a predetermined bulk composition X with two or more phases, is placed in a crucible, a thin foil or on a substrate made of a primary phase, then suspended on a wire to be equilibrated at controlled temperatures and gas atmospheres (maintained by mixture of pure gases such as CO, CO_2, H_2, Ar, SO_2 etc) or inside sealed ampoules. Predictions with preliminary thermodynamic models using FactSage package [2] are used to plan experiments. The furnace temperature is controlled to achieve overall accuracy within 5 K or better. The gas atmosphere is controlled to the actual accuracy of P_{O2} better than ± 0.1 Log (P_{O2}) units (~$\pm$0.02 LogP_{O2} can be achieved with special measures). The samples are quenched into iced water or salt solution so that the liquid phases are converted to glass or fine microcrystalline material, and the solid crystals existed at the temperature are frozen in place thus representing equilibrium phases existed at the temperature (see example of final microstructure in Figure 1). The sections are prepared, resulting microstructures are examined with optical and then Scanning Electron Microscopy (SEM) and the compositions of the phases (glass, microcrystalline and solids) are then measured using an electron probe X-ray microanalyser (EPMA) with Wavelength Dispersive Detectors (WDD) with accuracy within 1 wt % or better. Laser Ablation ICP-MS microanalysis technique is used for minor elements at low (ppm and ppb) concentrations with spatial resolution of ~30-50μm.

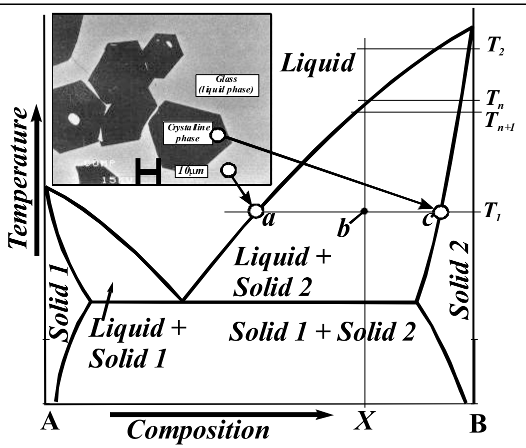

Figure 1. Hypothetical diagram to illustrate experimental technique for determination of phase equilibria.

The key advantage of this approach is that the accuracy of results are independent from the changes of bulk composition during the experiment (provided the achievement of equilibrium between phases is confirmed) since the compositions of phases are measured after rather than before the experiment thus eliminating uncertainties due to interaction with the containment material (crucible, substrate), vaporisation of some elements during equilibration, uncertainties in the initial mixture composition and the changes in phase compositions due to the gas / metal / matte / slag / solid(s) interactions. The small size (down to a several micron film) and direct exposure to gas and quenching media of the liquid slag /matte / metal phases equilibrated on solid substrates enhances achievement of a) equilibrium of condensed phases with the gas phase as well as b) high quenching rates, thus extending the applications to the systems where these factors are the limitations for research. The compositions of all liquid and solid solution phases at equilibrium are measured directly providing data for further thermodynamic modelling. The achievement of equilibrium and other factors affecting uncertainties can be directly investigated from microstructural analysis and compositional profiles at micro (~ <20μm) and macro (~ >20μm) scale measured with EPMA or other microanalysis techniques. The key tests to ensure the achievement of equilibrium include:

1. Changing the equilibration time to confirm that no further changes take place with time.
2. Confirming the chemical homogeneity of phases and samples.
3. Approaching equilibrium from different directions.
4. Analysing possible reactions taking place during equilibration.

Available analytical techniques including SEM imaging and EPMA analysis of the compositional gradients across the phases used in the present study are particularly effective for the analysis of possible signs of incomplete reaction pathways during equilibration.

None of the separate tests on their own can be taken as the final prove of the achievement of equilibria and the systematic and simultaneous application of all four tests is essential.

The equilibration / quenching / microanalysis approach to phase equilibrium determination has greatly extended the range of metallurgical systems that can be characterised. Experimental methodology is described in more details in previous publications [1, 3]. Examples of the application of this experimental approach can be found in a number of publications for various chemical systems, and a summary of earlier publications relevant to different chemical systems is given in Jak [3].

2.2. Thermodynamic modelling

Thermodynamic databases are developed through thermodynamic optimization that involves selection of proper thermodynamic models for all phases in a system, critical simultaneous evaluation of all available thermodynamic and phase equilibrium data and optimization of thermodynamic model parameters to obtain one self-consistent set best reproducing all experimental data as functions of temperature and composition.

In the thermodynamic "optimization" of a system, all available thermodynamic and phase equilibrium data for the system are evaluated simultaneously to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, the thermodynamic properties and the phase diagrams can be back-calculated. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be identified during the development of the model. These discrepancies can then be resolved through new experimental studies that, if possible, are undertaken in areas essential for further thermodynamic optimizations. Multicomponent data, if available, are used to derive and test low-order (binary and ternary) model parameters, and if multicomponent data for a system are lacking, the low-order parameters are extrapolated. In this way, the thermodynamic databases are developed and all the data are rendered self-consistent and consistent with thermodynamic principles. FactSage computer system [2] has been used by the authors for the thermodynamic modelling. The molten slag phase is modelled by the Modified Quasichemical Model [4] in which short-range-ordering is taken into account. Oxide solid solutions are described with a polynomial model or with the Compound Energy Formalism [5].

2.3. Integrated thermodynamic database development using modelling and experimental studies

The integrated combination of experimental and thermodynamic modelling studies carried out in parallel is an important factor in the present study to ensure high productivity and quality of research outcomes. The initial thermodynamic assessment is used a) to evaluate existing experimental data, b) to identify areas of importance for experimental research, c) to focus new experimental work to resolve discrepancies of previous or acquire new data, and d) to assist in detailed planning of the individual experiments in complex systems. There is usually a lack of experimental information to test model predictions in the multi-component slags and therefore multi-component databases are frequently developed on the basis of only binary and ternary data thus effectively extrapolating the low order binary and ternary parameters into a multi-component area without test. The present experimental program, in addition to the work on the binary and ternary systems, specifically focuses on multi-component systems in the composition and oxygen partial pressure ranges close to the important industrial slags. The thermodynamic model then is checked and corrected to agree with those multi-component measurements in the vicinity of the industrial slags. This is an important feature of the present study – the optimisation is performed in a number of cycles from binary and ternary to the multi-component systems and back so that binaries and ternaries are reoptimized to reach agreement also with the extensive data set in the multi-component area. Summary of the examples of the integrated experimental and thermodynamic modelling approach can be found in Jak [3].

3. Overview of results relevant to the non-ferrous smelting and recycling systems.

3.1. Example of experimental study in the Cu-Fe-O-S-Si system

The Cu-Fe-O-S-Si system is essential to copper and many other non-ferrous smelting and recycling processes. Present study on this system used experimental and overall integrated approach outlined above. Reactions taking place during equilibration between gas/slag/matte/solids phases are complex and substantial development of experimental methodology was required to achieve high reliability of results. Experiments were undertaken on tridymite or spinel substrates at fixed temperature and gas atmosphere with P_{O2} and P_{SO2} controlled by $CO/CO_2/SO_2$ gas mixtures. The smallest set of graphs but sufficient to describe measured compositions of all phases included i) P_{O2}, and S in matte and ii) "FeO", S and Cu in slag, all plotted as functions of Cu in matte (oxygen concentrations in matte and slag were not measured in this study). Pure oxide, sulfide and metal powders were mixed in carefully planned proportions to obtain slag and matte starting compositions based on the assumption of relatively fast equilibration achieved between condensed phases. Initial starting phase compositions and proportions of oxide, sulfide and metal powders were predicted with FactSage with preliminary database. The microstructures of the preliminary short experiments were carefully analyzed, compositions of slag and matte phases were plotted in graphs and compared to predicted, composition gradients at micro and macro scales were measured in all phases across samples and presented on the selected set of graphs. The trends of the compositional changes across phases and across samples were analyzed and this way key reactions taking place during equilibration were identified. The classification of phase microstructures was developed and introduced based on relative locations of phases. Figures 2 and 3 present example of non-equilibrium preliminary experiment in the Cu-Fe-O-S-Si system undertaken at 1200°C, P_{SO2}=0.25 atm and P_{O2}=$10^{-8.6}$ atm. The microstructure of this sample presented in Figure 2 illustrates different morphologies of matte dependent on relative locations to the gas and slag phase.

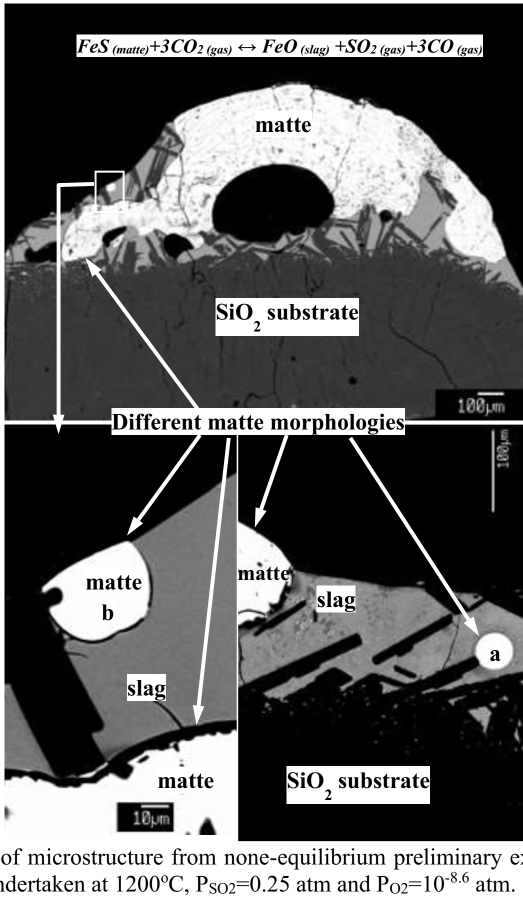

Figure 2. Example of microstructure from none-equilibrium preliminary experiment in the Cu-Fe-O-S-Si system undertaken at 1200°C, P_{SO2}=0.25 atm and P_{O2}=$10^{-8.6}$ atm.

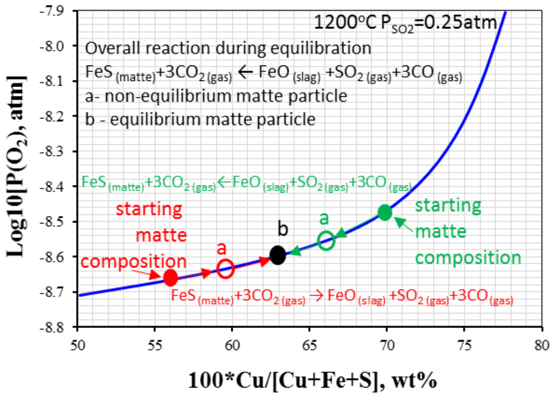

Figure 3. Schematic with oxygen partial pressure vs matte grade in the Cu-Fe-O-S-Si system at 1200°C and P_{SO2}=0.25 atm showing change of the matte and slag compositions in non-equilibrium samples during equilibration at fixed oxygen partial pressure $10^{-8.6}$ atm due to the mass exchange reaction FeS $_{(matte)}$+3CO$_2$ $_{(gas)}$ ↔ FeO $_{(slag)}$ +SO$_2$ $_{(gas)}$+3CO $_{(gas)}$.

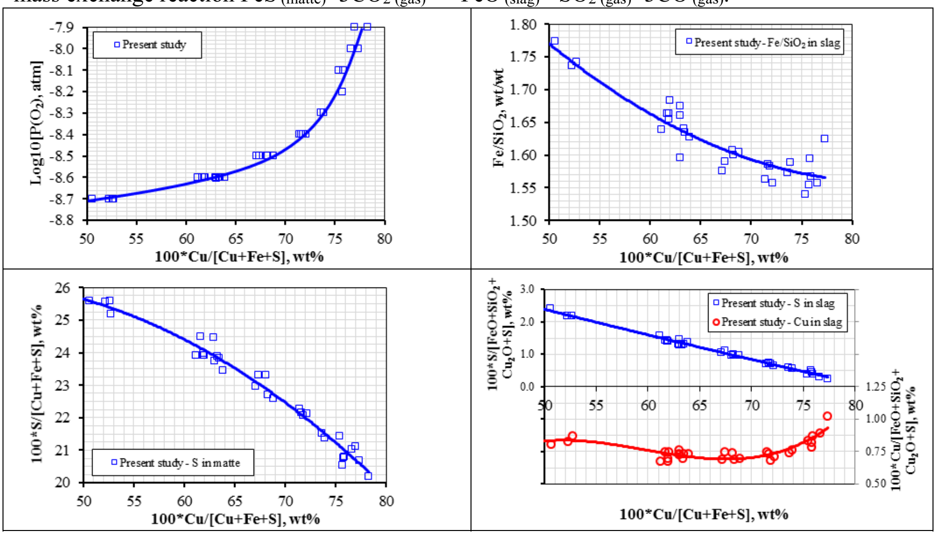

Figure 4. Set of graphs describing phase equilibria in the Cu-Fe-O-S-Si system between gas/slag/matte/tridymite at T=1200°C and P_{SO2}=0.25 atm.

The key overall mass exchange reaction between gas, slag and matte in this series of experiments was identified as FeS $_{(matte)}$+3CO$_2$ $_{(gas)}$ ↔ FeO $_{(slag)}$ +SO$_2$ $_{(gas)}$+3CO $_{(gas)}$ (1) (a number of other elemental reactions also have to be considered). The matte particle "a" completely surrounded by slag (see Figure 2) is blocked from the gas by the slag layer, and therefore the overall mass exchange reaction (1) requires a number of additional steps including gas-slag, diffusion of reactants and products through the slag phase and slag-matte reactions, so that the rate of the overall reaction (1) would be slow and the composition of the “a”-matte particle will be close to the initial matte composition and far from equilibrium (see schematic in Figure 3). The matte particle “b” on the surface of the slag is exposed to the gas, the overall reaction (1) would therefore progress fast, and the composition of the matte particle “b” would be close and eventually equal to the equilibrium matte composition – this is confirmed by longer experiments with starting matte composition located on both sides from but close to the final equilibrium point (see Figure 3). Identification of the key reactions was used to introduce a number of other experimental modifications such as substrate shape, initial mixture preparation (e.g. different proportions of metal/sulfide/oxide powders), master slag, master matte and other. Independent tests by other researchers were used in this study.

Figure 4 presents results for the equilibria between gas/slag/matte/tridymite phases in the Cu-Fe-O-S-Si system at T=1200°C and P_{SO_2}=0.25 atm obtained in this study using approaches outlined above.

Ranges of temperatures 1200-1300°C, SO_2 partial pressures 0.1-0.6 atm, matte grades 50-80wt%Cu, slag compositions from equilibria with tridymite to spinel, liquid phase assemblages (slag/matte, slag/metal and slag/matte/metal) are being investigated in the Cu-Fe-O-S-Si system with addition of Ca, Al, Mg as part of the overall research program. These experiments continue systematic characterization of the high-temperature chemistry of copper, lead and other non-ferrous smelting and recycling systems; summary of previous research is given in [3], more recent experimental work is published in [6-12].

3.2. Thermodynamic modelling results and integrated approach

A series of studies focused on phase equilibria and thermodynamics of the chemical systems important to the Cu pyrometallurgical production have been undertaken over recent years using the integrated experimental and thermodynamic modelling approach resulting in the development of thermodynamic database for copper-containing systems; the summary of previous studies is given in [3], more recent results are published in [13-22].

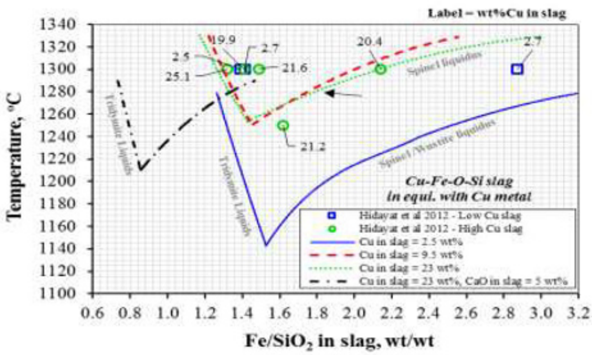

Figure 5. Comparison of the experimental data and thermodynamic model predictions in the Cu-Fe-O-Si system in equilibrium with metallic copper at fixed copper oxide concentrations in slag

and prediction of the effect of CaO addition on liquidus and solidus in the Ca-Cu-Fe-O-Si system in equilibrium with metallic copper.

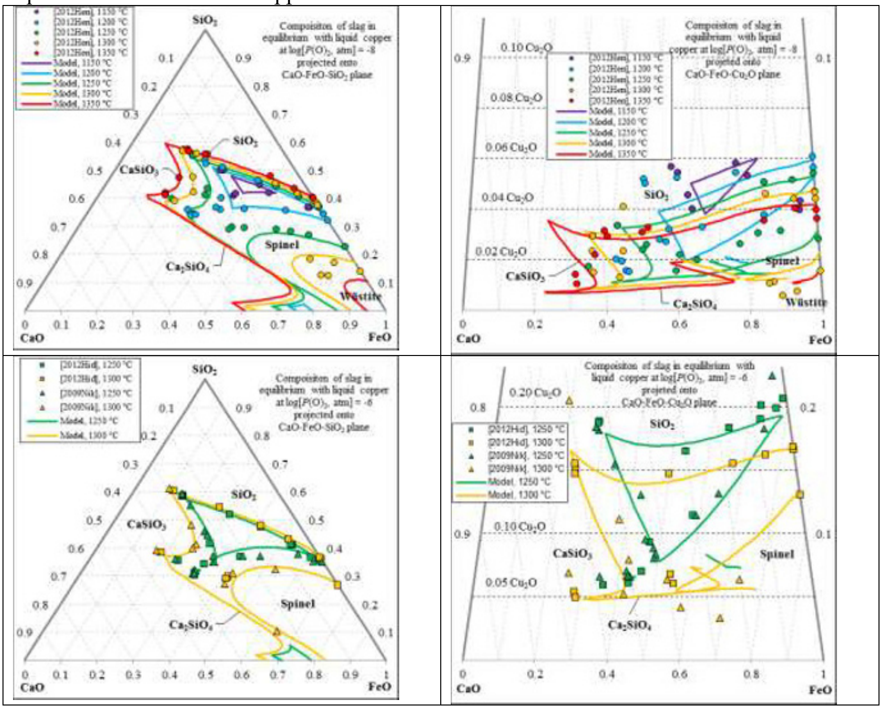

Figure 6. Comparison of the experimental data and thermodynamic model predictions in the Ca-Cu-Fe-O-Si system in equilibrium with metallic copper and gas at fixed oxygen partial pressures of 10^{-8} and 10^{-6} atm.

Figure 5 illustrates an example of comparison of thermodynamic model predictions with the experimental results on the Cu-Fe-O-Si system in equilibrium with metallic Cu at conditions relevant to the direct to blister production [6]. Figure 6 provides an example of study on multi-component system Ca-Cu-Fe-O-Si system in equilibrium with metallic Cu [6, 13]. Good agreement between experimental data and FactSage predictions with the new thermodynamic database is demonstrated in these figures.

Integrated research program on the development of multi-component thermodynamic database ranges from a) the work on low order (binary and ternary) systems that are particularly important foundation for thermodynamic modelling to b) the investigations of the multi-component systems close to the industrial slags – the latter are used directly in industrial practice as well as provide an essential test for the development of the multi-component thermodynamic model.

Example of the application of thermodynamic database along with the FactSage package is given in Figure 5 that gives predicted effect of fluxing with CaO to reduce liquidus and solidus in the slag relevant to the direct-to-blister copper smelting. Predictions show that although addition of CaO results in the significant decrease of the solidus temperatures, the shift of the spinel liquidus to the lower Fe/SiO_2 range indicates at a possible need to increase addition of SiO_2 flux. The thermodynamic model can now be used to evaluate the optimum combination of temperature, flux additions and other thermochemical parameters to reach required operational criteria.

4. Characterization of minor elements distribution coefficients – application of the EPMA / Laser Ablation ICP-MS microanalysis

Present research program is further extended to characterize distribution coefficients of minor elements such as As, Pb, Zn, Sn, Sb, Bi, Au, Ag between slag, matte and metal phases in the non-ferrous system Cu-Fe-O-S-Si with addition of minor slagging elements Al, Ca, Mg. The distribution coefficients for some elements (e.g. Ag, Au) are far from 1:1 resulting in very low concentrations in some phases. The limitation of the research in this direction is the minimum detection limit and spatial resolution of the available quantitative microanalysis techniques. EPMA cannot routinely provide required accuracy at elemental concentration of ppm (parts per million) level. The laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) microanalysis technique provides the necessary low minimum detection limits [11]. Present research program is extended to develop a combined EPMA / LA-ICP-MS methodology to measure concentrations of elements in slag, matte and metal phases down to ppb levels [11]. Figure 7 demonstrates recent results [11] on the distribution coefficients of Ag and Au between slag and metal (wt% Me in slag / wt% Me in matte, where Me=Ag or Au) vs matte grade in the sample with slag/matte/metal/tridymite 4 phases in equilibrium at 1200°C in the Cu-Fe-O-Si system with addition of Ag and Au minor elements.

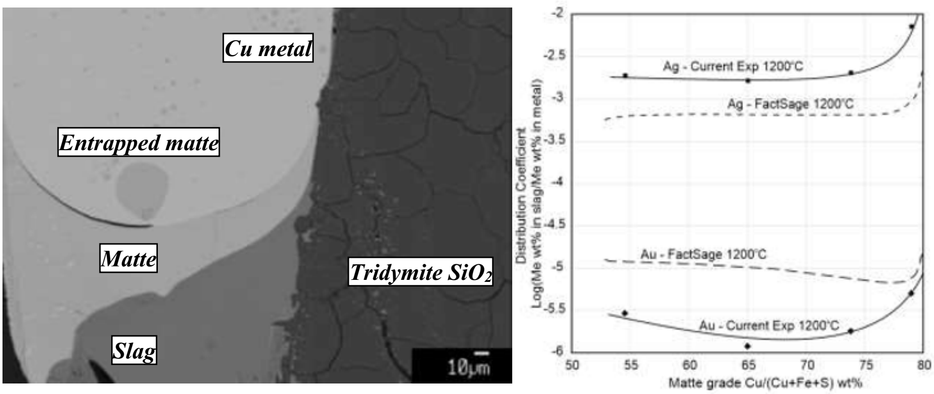

Figure 7. a) Microstructure of and b) distribution coefficients of Ag and Au between slag and metal vs matte grade wt %Cu/[Cu+Fe+S] in the sample with slag/matte/metal/tridymite 4 phases in equilibrium at 1200°C in the system Cu-Fe-O-Si with addition of Ag and Au minor elements [11].

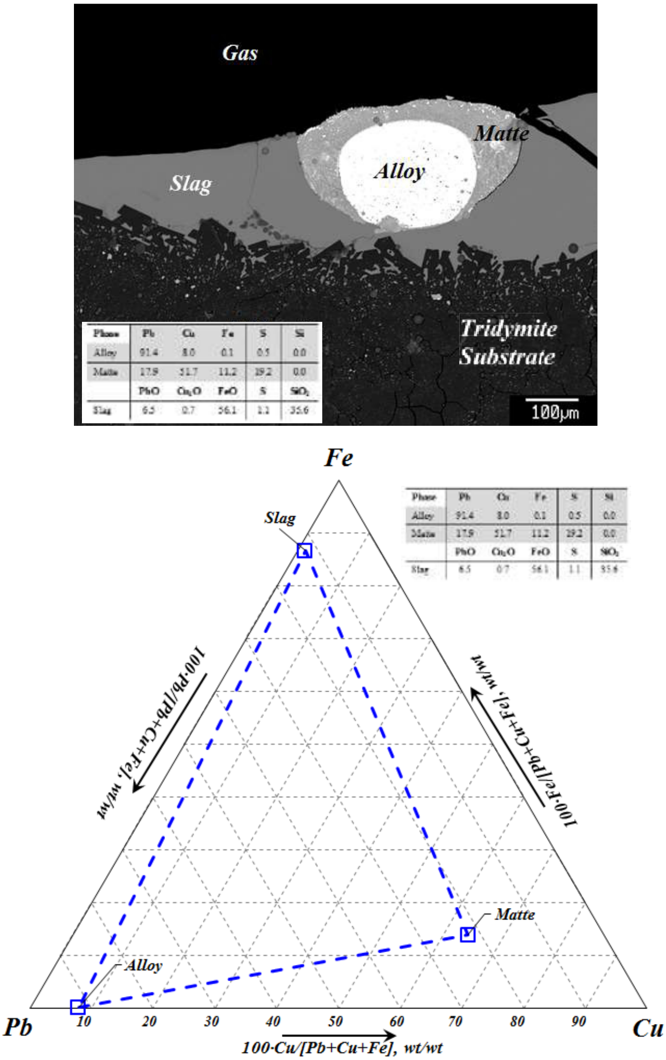

Figure 8. Back-scattered image of microstructure (top) and projection of phase compositions in the slag/matte/alloy/tridymite sample in the Cu-Fe-O-Pb-S-Si system equilibrated in the SiO_2 ampoule at T=1250°C for 18h.

5. Further research on the Pb-Cu-Zn-S-containing systems

The research has recently been extended to characterize the Pb-Cu-Zn-S-containing systems. Previous research on the Pb-Zn-containing systems was undertaken on the oxide-only systems PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2 with addition of Al_2O_3 and MgO in two extreme conditions – in air and in equilibrium with metallic iron. Thermodynamic database for the Pb-Zn-O-containing slag developed nearly two decades ago [23] used models available at that time. Many improvements in experimental and modelling techniques have been made and are being implemented now to characterize the thermo-chemistry of the Pb-Cu-Zn-S-containing slag / matte / metal / speiss systems of particular importance to non-ferrous and recycling systems.

Figure 8 presents the microstructure and projection of phase compositions in the sample in the Cu-Fe-O-Pb-S-Si system equilibrated in the SiO_2 ampoule at T=1250°C with complex slag, matte and metal alloy phases in equilibrium. These experiments provide important data on the tridymite liquidus of the complex slag as well as on the characterization of these complex systems and partitioning of Pb, Cu, Fe and S between phases. Results of these experiments are critical for further development of the thermodynamic database.

6. Conclusions

Advanced experimental and thermodynamic modelling techniques are continuously developed to characterize the thermochemistry of complex non-ferrous smelting and recycling systems. There is an opportunity now to use these powerful outcomes to improve metallurgical operations. The combination of several related research and development activities is believed to be the most efficient and promising approach that should include:
a) continuous laboratory-based fundamental and applied experimental research,
b) theoretical modelling integrated with experimental research,
c) plant tests and experiments, and
d) systematic implementation program combining collaborative efforts of technologists and researchers.

7. Acknowledgements

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