

Oxygen activity measurements in simulated converter matte

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It should be possible to use an oxygen probe to follow iron removal during converting, if local equilibrium is established between iron in the matte and the iron oxides in the fayalitic slag. The oxygen activity is expected to increase strongly as the iron content of the matte decreases (and the iron activity in the matte drops) while the iron oxide activity in the slag remains constant. To test this idea, oxygen activities were measured in synthetic mattes (made up of mixture of Cu_2S , FeS and Ni_3S_2) when in contact with silica saturated SiO_2 - FeO slags, and silica and (initially) magnetite saturated SiO_2 - FeO - Fe_3O_4 slags. The measurements were performed on laboratory scale at 1250°C , using an oxygen probe consisting of a stabilized zirconia electrolyte and Fe/FeO reference, and containing the sample in a silica crucible. Electrical contact to the matte was by means of a platinum wire. The measured oxygen activity was sensitive to the iron content of the matte, and insensitive to the composition of the gas atmosphere over the melt. The measured oxygen activity was generally close to that predicted by FactSage calculations. This indicates that such oxygen activity measurements could be useful to monitor iron removal during converting of nickel-copper-iron mattes.

Background

Expected relationship between oxygen activity and iron content of matte

The idea tested in this work is that the activity of oxygen, as established by reaction between the slag and the matte, should be measurable with an electrochemical probe, and that the oxygen activity should increase as the iron content of the matte decreases during converting. The rationale behind these ideas is stated briefly below.

Measurability of oxygen activity

The principle of using an electrochemical oxygen probe in this application is that dissolved oxygen in the matte equilibrates with oxygen anions on one surface of the solid electrolyte (oxygen anion conductor); a similar equilibrium is set up at the other surface of the electrolyte, where the oxygen activity is different, and controlled by means of a buffer (reference). Because of the difference in oxygen activity at the two surfaces of the electrolyte, a potential difference arises between electronic conductors at the two surfaces. This voltage is given by:

$$E = (RT/4F) \ln \left(p_{\text{O}_2}^{\text{matte}} / p_{\text{O}_2}^{\text{reference}} \right) \quad [1]$$

where E is the voltage difference, R is the ideal gas constant, T is the absolute temperature, F is Faraday's constant, and $p_{\text{O}_2}^{\text{matte}}$ and $p_{\text{O}_2}^{\text{reference}}$ are the partial pressures of oxygen in gas phases, which would be in equilibrium with the matte and with the reference respectively. (Note that Equation [1] neglects the effects of electronic conduction through the solid electrolyte; this is valid for the zirconia probe used here and for the relatively high measured oxygen activities.)

Oxygen probes which are based on this principle are used widely in the steel industry. The application, which was

tested in this work is similar, in that the matte contains dissolved oxygen (as does liquid steel), and that the matte is an electronic conductor that forms one of the electrodes of the voltage measurement circuit (as does the liquid steel).

Such measurements have been performed before, for mattes in copper processing (Taskinen *et al.*, 2001). The work presented in this paper tested whether such measurements are possible—on laboratory scale—for Fe-Ni-Cu-S mattes.

An essential part of this measurement is the reference; in this work, an Fe/'FeO' reference was used. Initial measurements with the more conventional Cr/ Cr_2O_3 reference showed this to give unstable and incorrect readings for the experimental conditions used. While the potential of the Fe/FeO reference is less exactly defined (since wüstite is not a stoichiometric oxide), this reference was found to give stable readings, and gave the correct value for the oxygen activity established by the combination of liquid Cu and liquid Cu_2O at 1250°C (Taskinen, 1984).

The oxygen probes were constructed with MgO-stabilized zirconia electrolyte tubes. The tubes were 50 mm long, had an outside diameter of 6 mm and an inside diameter of 5 mm, and were closed at one end. The reference mixture consisted of pure iron powder and powdered wüstite; the wüstite was prepared by decomposition of iron oxalate at 1000°C . An iron wire formed the electrical contact to the reference mixture; the end of the tube through which the iron wire passed was sealed with alumina cement.

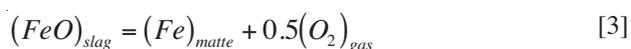
Expected effect of iron content of matte on oxygen activity

During converting of the Fe-Ni-Cu-S matte iron and sulphur are removed through reaction with injected oxygen, according to the coupled reactions:



Since converting removes iron, from a typical level of 40% (by mass) before converting, to 1–3% (by mass) after converting (Jones, 1999), it is expected that the activity of dissolved iron in the matte would decrease as converting proceeds. This change is quantified by Figure 1, which shows the calculated activity of dissolved iron (pure liquid iron as reference state), for Fe-Ni-Cu-S mattes of different iron contents. As for all the other equilibrium data presented in this paper, the values shown in Figure 1 were calculated using FactSage (v.5.4.1) (Bale *et al.*, 2002), with the ‘FTmisc-matte’ solution model for the matte (for other calculations involving fayalitic slag the ‘FToxid-SlagA’ slag solution model was used in addition). The values in Figure 1 are shown for two different Ni:Cu mass ratios in the matte (1.5 and 2.0, values chosen to bracket the range of actual matte compositions), and for three different scenarios regarding the sulphur content of the matte. The sulphur contents are given relative to the sulphur content, which would obtain if the matte were a mixture of stoichiometric FeS, Cu₂S and Ni₃S₂; based on published analyses (Jones, 1999), the sulphur content of mattes before converting (‘green matte’) is close to that of mixtures of such stoichiometric sulphides (that is, $S/S_{stoich} \approx 1$), whereas that of converter matte (‘white matte’) is significantly lower, corresponding to $S/S_{stoich} \approx 0.8$. (Apart from the expected strong effect of iron content on the activity of iron, the extremely strong effect of sulphur on the activity of iron is also clear from Figure 1.)

One of the assumptions behind the measurements presented in this paper is that the activity of dissolved oxygen in the matte is controlled by local equilibrium between the slag and matte, according to the reaction



At 1250°C, the equilibrium constant of this reaction is $K = 2.03 \times 10^{-6}$, if both FeO and Fe activities are represented with pure liquid reference states.

Since the converter slag operates close to silica saturation, this means that the FeO activity is approximately constant (although the presence of trivalent iron in the slag will change the FeO activity). If the slag is approximated as a binary SiO₂-FeO mixture, the FeO activity (liquid reference state) in silica-saturated slag is 0.34.

From these values of the equilibrium constant and FeO activity, and with the Fe activities as given in Figure 1, the expected change in oxygen activity with Fe content was calculated, with the results presented in Figure 2. A sharp increase in oxygen activity is predicted as the Fe content of the matte is decreased in the matte, with an increase in oxygen activity of approximately two orders of magnitude when the Fe content is decreased from 10% to 1% (typical end-point iron contents are in the range 1.5–6%; Jones, 1999).

However, the expected change in oxygen activity is less than this, since—as noted above—the ratio S/S_{stoich} changes from 1 at high Fe contents to 0.8 at the endpoint of converting. This shift of relative sulphur content—and its associated effect on the iron and oxygen activities—was predicted by assuming that the matte and slag equilibrate with a gas in which the partial pressure of SO₂ is 0.1 atm; this was also the approach used by Yazawa (1974) to

predict changes in oxygen activity in converting of Cu-Fe-S mattes. The appropriate sulphur content of the matte which gives $p_{SO_2} = 0.1$ atm at each Fe content of the matte was found by assuming equilibrium between the matte, silica-saturated FeO-SiO₂ slag, and gas containing SO₂ and an inert diluent; the sulphur content was adjusted manually until the desired activity of SO₂ was found. The matte sulphur contents, which satisfy this requirement are shown in Figure 3, which also gives the reported S analyses of actual converter mattes; these correspond quite well to the calculated value of 21%S at 1%Fe.

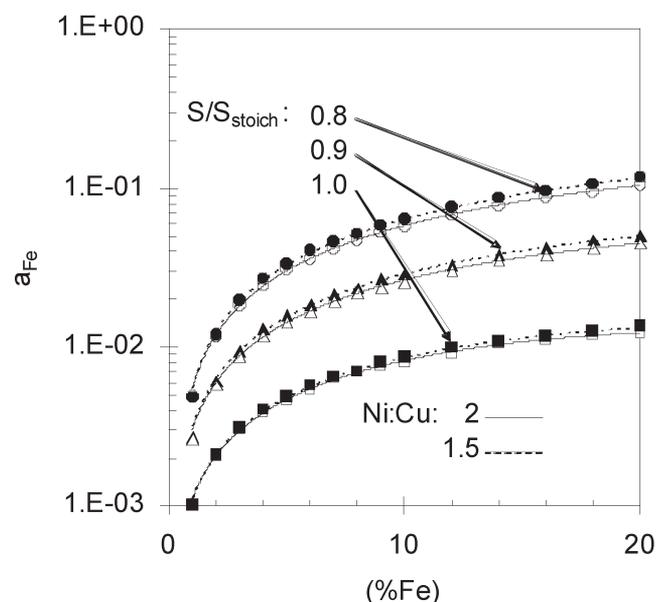


Figure 1. Calculated activity of Fe (pure liquid Fe reference state) in Fe-Ni-Cu-S mattes at 1250°C, for two mass ratios of Ni to Cu in the matte, and for three sulphur contents relative to that in a mixture of stoichiometric FeS, Cu₂S and Ni₃S₂

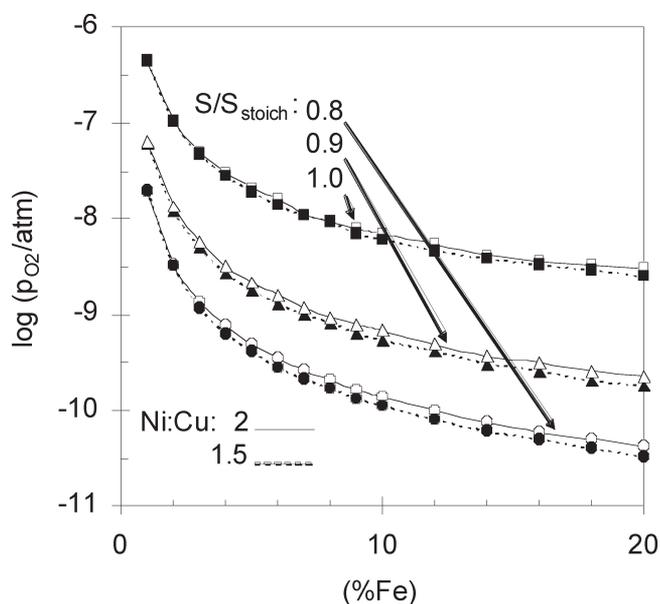


Figure 2. Calculated oxygen activity for equilibrium between Fe in Fe-Ni-Cu-S mattes and SiO₂-saturated FeO-SiO₂ slag at 1250°C, for two mass ratios of Ni to Cu in the matte, and for three sulphur contents relative to that in a mixture of stoichiometric FeS, Cu₂S and Ni₃S₂

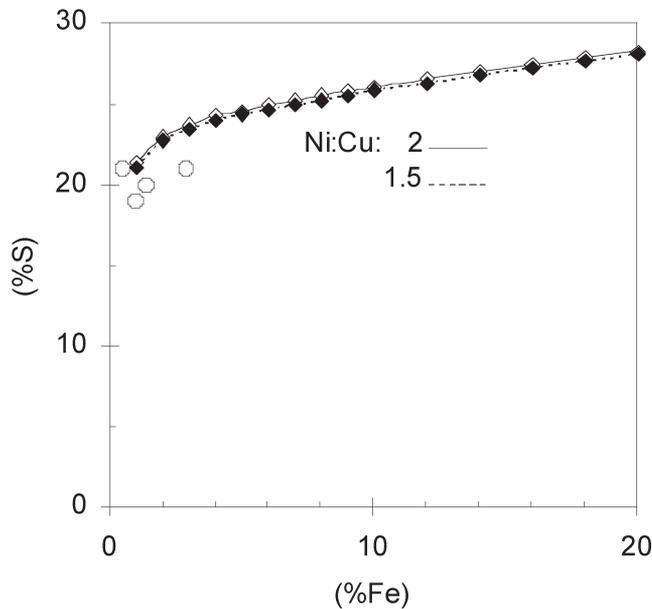


Figure 3. Calculated S content of Fe-Ni-Cu-S mattes which maintain $p_{\text{SO}_2} = 0.1$ atm in equilibrium with SiO_2 -saturated FeO-SiO₂ slag, at 1250°C. The round data points give the end-point compositions of converter mattes for different operations (Jones, 1999)

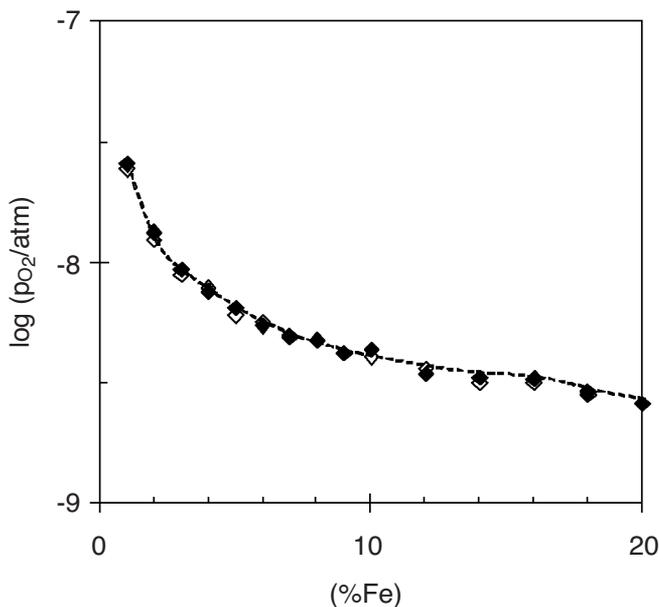


Figure 4. Calculated oxygen activity for equilibrium at 1250°C between Fe in Fe-Ni-Cu-S mattes, SiO_2 -saturated FeO-SiO₂ slag, and gas with $p_{\text{SO}_2} = 0.1$ atm (giving the S contents as in Figure 3). Open symbols are for mattes with a Ni:Cu mass ratio of 2, and filled symbols for a Ni:Cu ratio of 1.5

When using the predicted change in matte sulphur content (of Figure 3), the change in iron activity—and hence p_{O_2} —during converting is not nearly as strong as at a constant $\text{S}/\text{S}_{\text{stoich}}$ ratio, as Figure 4 reveals. However, the predicted change in oxygen activity if the Fe content of the matte decreases from 10% to 1% remains significant, at just less than an order of magnitude. Such a difference would be measurable with an oxygen probe: as Equation [1] shows, a factor 10 change in oxygen activity corresponds to a difference in measured voltage of 76 mV (at 1250°C).

From these theoretical considerations, it appears that oxygen activity measurement is a feasible method to detect the end point in converters for Fe-Ni-Cu-S mattes. The experimental work, which is reported in the rest of this paper, tested whether the oxygen activities are indeed measurable, for artificial converter mattes.

Experimental approach

The experimental apparatus used in this study consisted of the following:

A zirconia tube electrolyte (4 mm I.D., 6 mm O.D., and 50 mm in length, closed at one end) containing Fe and FeO (as oxygen reference), with an iron rod (2 mm diameter) as electrical lead. The back of the zirconia tube (where the iron rod exited) was sealed with alumina cement and the rod was protected with a silica tube.

Platinum wire (0.5 mm diameter), shielded with a mullite tube, was immersed in the matte to complete the electrical circuit.

The use of iron and platinum connecting wires implies that a thermal EMF was included in the measured potential difference between the oxygen probe and the matte. This offset was removed by subtracting the thermal EMF, which was measured separately (Figure 5).

A thermocouple (Pt-13 per cent Rh) was used to measure the temperature; the tip of the thermocouple was positioned approximately 1 cm to the side of the crucible.

Gas (Ar or a CO/CO₂/SO₂ mixture) was supplied through a 6 mm O.D., 4 mm I.D., silica tube. The tip of the gas inlet tube was approximately 2 cm from the top of the crucible.

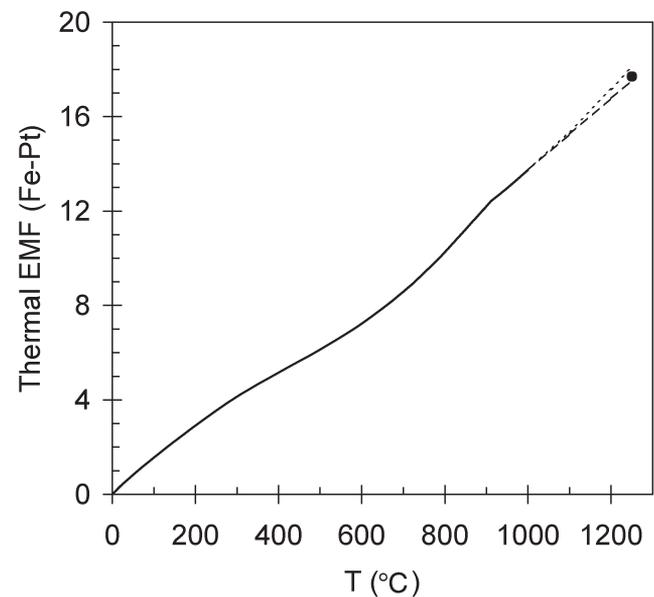


Figure 5. Thermal EMF between iron and platinum, as a function of the hot junction temperature, with the cold junction at 0°C.

This was used to correct the measured potential difference between the oxygen probe and the matte. The solid line gives the calculated thermal EMF based on the published Seebeck coefficients of Fe and Pt (Hellwege and Olson, 1989). Since the Seebeck coefficient for Fe could not be found for temperatures higher than 1000°C, the data were extrapolated by assuming no change in the Seebeck coefficient at higher temperatures (upper broken line), and assuming a constant slope of thermal EMF with temperature over the range 950°C–1250°C (lower broken line). The measured value (data point for 1250°C) agrees well with the calculated values

The potential effect of gas composition was evaluated in separate measurements with mattes containing 3.7%, 6.0% and 6.4% Fe (mass percentages). For a given matte composition, the measured oxygen activity was the same whether the gas was Ar or a CO/CO₂/SO₂ mixture, as the results in Table I show. This must reflect slow reaction between the gas and slag, compared with the rate of the slag-matte reaction. For this reason, all the measurements which are reported in this paper were performed under an argon atmosphere.

The sample was contained in a silica crucible. Equal masses of silica-saturated fayalitic slag and matte were used, with a total sample mass of 20 g. (Preliminary measurements with a smaller total mass 10 g were found to give oxygen activity results which were insensitive to matte composition, presumably because of inadequate ionic contact between the probe, matte and slag.)

The matte and slag were prepared in the laboratory from chemically pure or high quality commercial materials. Ni₃S₂, Cu₂S and FeS for the matte components were premelted in a silica crucible. Slag with (62 mass% FeO-38 mass% SiO₂) was premelted by fusing FeO powder and SiO₂ powder under argon in an iron crucible. SiO₂ was added in slight excess of the saturation concentration. After cooling, the premelted slag and matte were milled separately and charged to the crucible as powders. In some runs, Fe₂O₃ was added to the slag, to ensure a starting slag composition at magnetite saturation (in these cases, a molar ratio of ferrous to ferric ions of 2:1 was used in the starting slag, since this corresponds to the calculated ratio at dual magnetite and silica saturation at 1250°C). Slag and matte powders were mixed intimately. After placing the silica crucible in the furnace, the working tube was flushed with Ar for 30 min. The furnace was heated to 1250°C at 100°C per hour.

After set periods (1h, 2h, 3h and 4h), samples were aspirated into a silica tube which was introduced through a sampling hole. At the same times, oxygen probe measurements were taken, using the zirconia-based probe and an electrometer with high input impedance.

At the end of the experiment the gas mixture was replaced with Ar, and the crucible cooled with the furnace. Each run was performed twice for a given matte composition.

Samples were removed from the furnace and carefully separated from the silica crucible. The samples were ground in a mortar to obtain small pieces and then mounted for further energy-dispersive X-ray EDX microanalysis (EDX) in a scanning electron microscope (SEM), and also in an electron probe microanalyser (WDS). As will be shown below, the solidified matte consisted of several phases, and an average matte composition was determined by microanalysis; this matte composition served as the main independent variable in this work, and was also used as an input in FactSage calculations of the expected oxygen activity (using the procedure as outlined above).

Results

Oxygen activity

The experimental results are summarized in Table II, and presented graphically in Figure 6. The expected trend of significantly increasing oxygen activity at lower Fe levels in the matte is observed, especially for Fe levels below 3%. The measured oxygen activities agree reasonably well with the calculated values, and generally better so for the slag which contained some ferric ions. For the latter set of measurements, it is clear that reaction between the slag and the matte had taken place: for slag which is doubly saturated with silica and magnetite (the starting slag used in

Table I
Measured voltage difference (corrected for thermal EMF) between mattes of different compositions (which were in contact with silica-saturated fayalite slag), and an Fe/FeO reference, at 1250°C, for cases where the gas atmosphere was pure argon and a CO/CO₂/SO₂ mixture respectively. Partial pressures in the mixture were: SO₂ (0.44 atm), CO₂ (0.45 atm) and CO (0.02 atm). The expected p_{O₂} and EMF if equilibrium with the gas were achieved would be 3.6×10⁻⁸atm and -294 mV respectively

(%Fe) _{matte}	Measured EMF (mV)	
	CO-CO ₂ -SO ₂	Ar
6.4	- 194	- 196
6.0	- 229	- 230
3.7	- 232	- 234

Table II
Summary of experimental results, showing the average matte compositions (as determined by micro-analysis, with 95% confidence intervals), with the measured oxygen activity, and the oxygen activity predicted for equilibrium of matte with the average composition with silica-saturated FeO-SiO₂ slag at 1250°C. Slags are predicted to be saturated with magnetite for the oxygen activities which are shown in bold

Slag type	Matte composition (mass percentages)				log (pO ₂ /atm)	
	Fe	Cu	Ni	S	Measured	Predicted
FeO-Fe ₂ O ₃ -SiO ₂	6.4±0.4	23.7±2.7	48.6±2.0	21.3±2.4	-9.89	-9.57
	5.0±0.6	25.0±3.8	48.7±3.8	21.2±1.4	-9.52	-9.34
	3.8±0.3	22.4±4.1	50.7±2.7	23.0±1.7	-9.12	-8.57
	2.6±0.4	21.6±2.3	52.9±2.9	23.0±3.2	-8.48	-8.21
	0.8±0.2	24.5±5.7	49.3±2.3	25.5±4.1	-6.45	-7.17
FeO-SiO ₂	6.4±1.0	22.8±1.8	48.9±2.8	21.8±2.1	-9.49	-9.45
	6.0±1.0	22.5±2.1	50.7±1.7	21.5±1.7	-8.99	-9.48
	3.7±1.1	21.5±1.9	52.8±2.8	21.9±2.7	-8.83	-8.88
	2.8±0.5	22.8±2.5	52.0±3.3	22.4±3.0	-8.52	-8.45
	2.2±0.2	23.5±3.5	52.2±2.2	22.1±2.0	-8.43	-8.29
	0.7±0.2	22.9±3.3	51.1±1.3	25.4±3.7	-7.09	-7.22

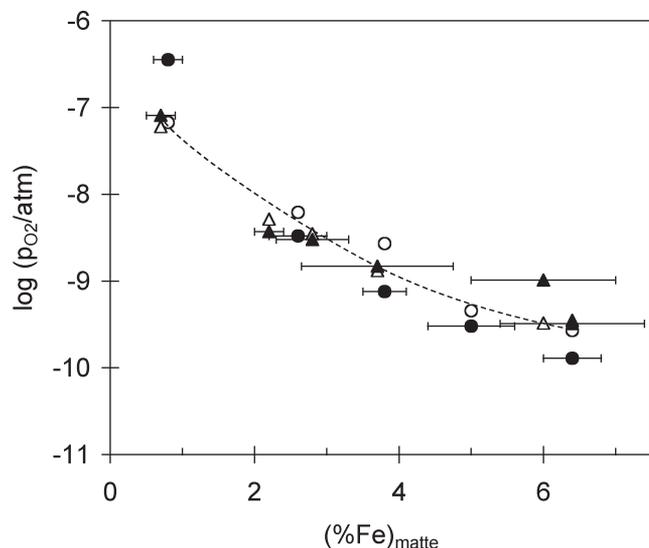


Figure 6. Comparison of measured and predicted dependence of the oxygen activity on the Fe content of the matte. Open symbols give the predicted oxygen activities, for the average matte compositions given in Table II. Closed symbols give the measured oxygen activities; the horizontal error bars give the 95% confidence intervals on the matte iron content. Triangles are for experiments with the FeO-SiO₂ slag, and circles for the FeO-Fe₂O₃-SiO₂ slag

these experiments), the equilibrium oxygen activity is approximately $\log(p_{O_2}/\text{atm}) = -7$. This is higher than the measured values, except for the experiments with the lowest Fe contents of the matte (0.7% and 0.8%), where similar oxygen activities were measured. (For the conditions of these two experiments, the equilibrium calculations indicated that the slag is saturated with magnetite.)

These results demonstrate the principle of monitoring the Fe content of converter matte through measurement of oxygen activities; it would take a separate study to test whether this would be feasible in an operating plant.

Phases in solidified matte

The equilibrium calculations that were used here to predict the oxygen activities can also be employed to predict phase equilibria during solidification of the matte. This is of practical interest, for example to the formation of an alloy phase during slow cooling of converter matte (Jones, 1999). To evaluate whether these equilibrium calculations give reasonable results, the phase changes for one matte composition (6.4% Fe, 22.8% Cu, 48.9% Ni, 21.8% S) was predicted with FactSage, and compared with the actual phases as found by X-ray diffraction and scanning electron micrography. The microstructure of this sample is shown in Figure 7. The three major phases visible in this micrograph (digenite, heazlewoodite, and alloy) were also identified by X-ray diffraction. The equilibrium calculation (Figure 8) also predicts these phases to be present below the solidus temperature.

Conclusion

Laboratory measurements have demonstrated that the oxygen activity in simulated converter matte containing Ni, Cu, Fe and S tracks the iron content of the matte, with the measured oxygen activities close to those predicted for

equilibrium with FeO-SiO₂ slag. Equilibrium calculations with FactSage have been useful to predict both these oxygen activities, and the phase changes during solidification of converter matte.

References

- BALE, C.W., CHARTRAND, P., DEGTEROV, S.A., ERIKSSON, G., HACK, K., BEN MAHFOUD, R., MELANÇON, J., PELTON, A.D., and PETERSEN, S. FactSage Thermochemical Software and Databases. *Calphad*, vol. 26, 2002. pp. 189–228.

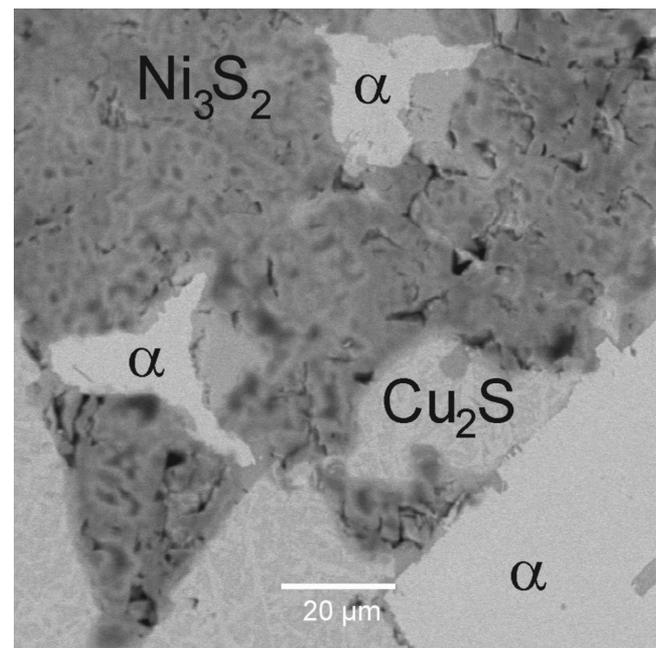


Figure 7. Scanning electron micrograph (backscattered electron image) of solidified matte containing 6.4% Fe, 22.8% Cu, 48.9% Ni, and 21.8% S. α indicates Fe-Ni alloy, Cu₂S digenite, and Ni₃S₂ heazlewoodite

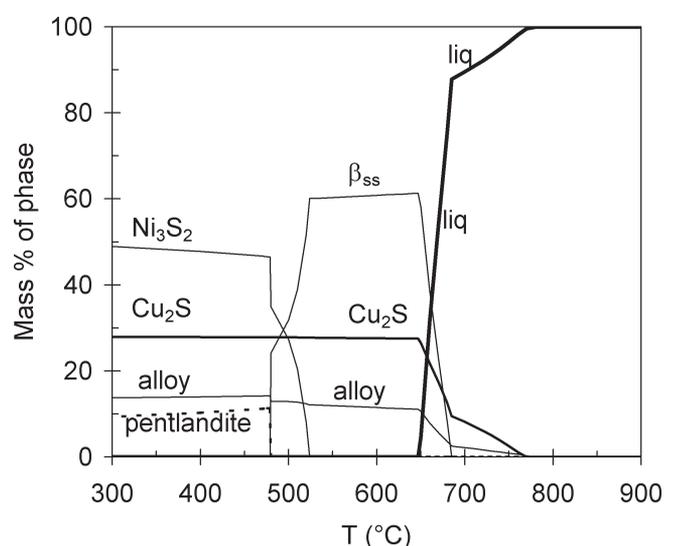


Figure 8. Predicted change in phase composition of the matte of which the microstructure after solidification is shown in Figure 7. Note that β_{ss} is the solid-solution based on Ni₃S₂ which is stable at higher temperatures. Predicted using FactSage

- HELLWEGE, K.-H. and OLSON, J.L. (eds.) Metals: electronic transport phenomena. Landolt-Bornstein Numerical data and functional relationships in science and technology, New Series, Group III, *Crystal and solid state physics*, vol. 15. Springer, Berlin, 1989.
- JONES, R.T. Platinum smelting in South Africa. *South African Journal of Science*, vol. 95, 1999. pp. 525–534.
- TASKINEN, P. Thermodynamics of liquid copper-oxygen alloys at 1065–1450°C. *Scandinavian Journal of Metallurgy*, vol. 13, 1984. pp. 75–82.
- TASKINEN, P., SEPPÄLÄ, K., LAULUMAA, J., and POIJÄRVI, J. Oxygen pressure in the Outokumpu flash smelting furnace—Part 1: Copper flash smelting settler. *Transactions of the Institutions of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy*, vol. 110, 2001. pp. C94–C100.
- YAZAWA, A. Thermodynamic considerations of copper smelting. *Canadian Metallurgical Quarterly*, vol. 13, 1974. pp. 443–453.