

CHAPTER IV

EXPERIMENTAL RESULTS

IV. 1. Results overview

This chapter presents the experimental results of the present investigation. The main variable in the investigation was the oxygen partial pressure. The temperature was maintained constant during all the experiments at 1250°C, and the total pressure was 0.86 atm, average pressure in Pretoria.

The initial oxygen activity was estimated from the data using FACTSAGE.

The expected oxygen activity was obtained by using thermodynamic calculations for the

reaction $\text{Fe} + \frac{1}{2} \text{O}_2 = \text{FeO}$ with $k = \frac{a_{\text{FeO}}}{a_{\text{Fe}} P_{\text{O}_2}^{0.5}} = 498080$ (temperature = 1250°C, FACTSAGE).

The activity of FeO was found to be 0.35 (liquid reference state) for SiO₂ saturated FeO-SiO₂ at 1250°C. The activity of iron in matte was calculated using FactSage.

All the measurements reported in this chapter were performed with Ar as flushing gas.

IV.2.Results of different tests

The tests were performed with two different slags:

One set used slag containing SiO₂ and FeO, and in the other case Fe₂O₃ was added to the slag.

Fe₂O₃ was added to yield a Fe²⁺: Fe³⁺ ratio of 2:1. Thus corresponds to magnetite saturation.

The hematite was added to test the effect of ferric ions on the measured oxygen potential.

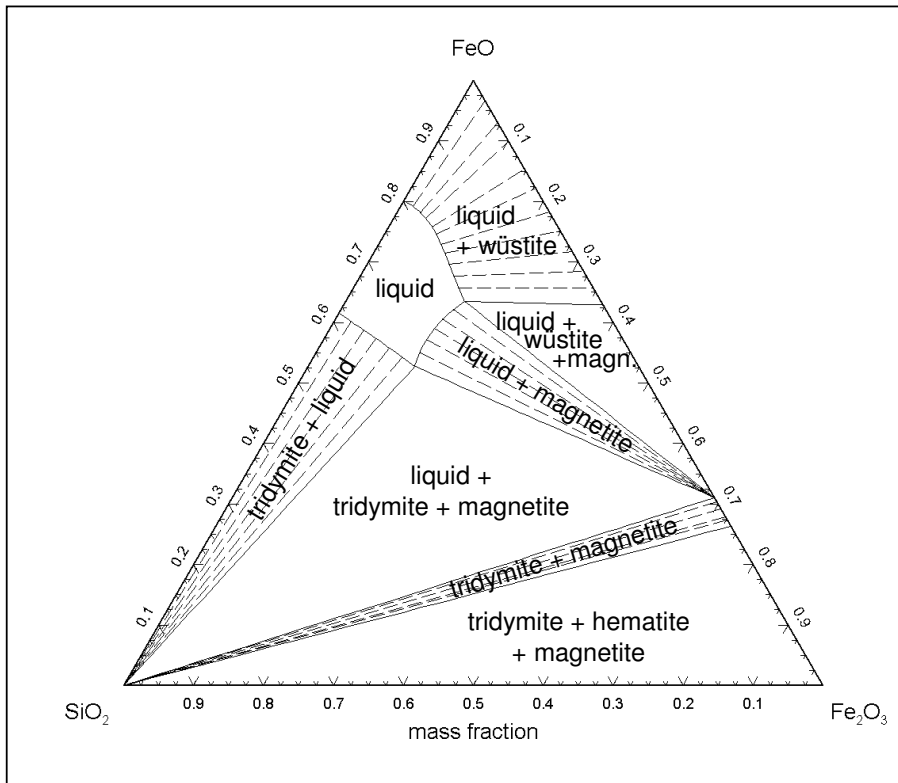


Figure 4-1. Phase diagram for FeO-SiO₂-Fe₂O₃ at 1250°C (FACTSAGE)

IV.2.1. FeO-SiO₂ slag

Results obtained with different matte composition varying between 8.8 wt% and 1 wt% iron content, a slag composition of 30 Wt% SiO₂ and 70Wt% FeO in argon at 1250°C are presented in Appendix- B.

In the figures in this chapter, ‘oxygen calculated’ expresses the theoretical calculations performed with FACTSAGE (matte was assumed to be in a liquid phase and the initial composition used was the matte weighed in the laboratory) to determine the expected oxygen activity. Meas A and B express the measurements performed with same matte composition with different sample weight: 5g and 10g respectively. The horizontal and vertical error bars on figure 4.2 show the range of analysed iron content and oxygen activity respectively.

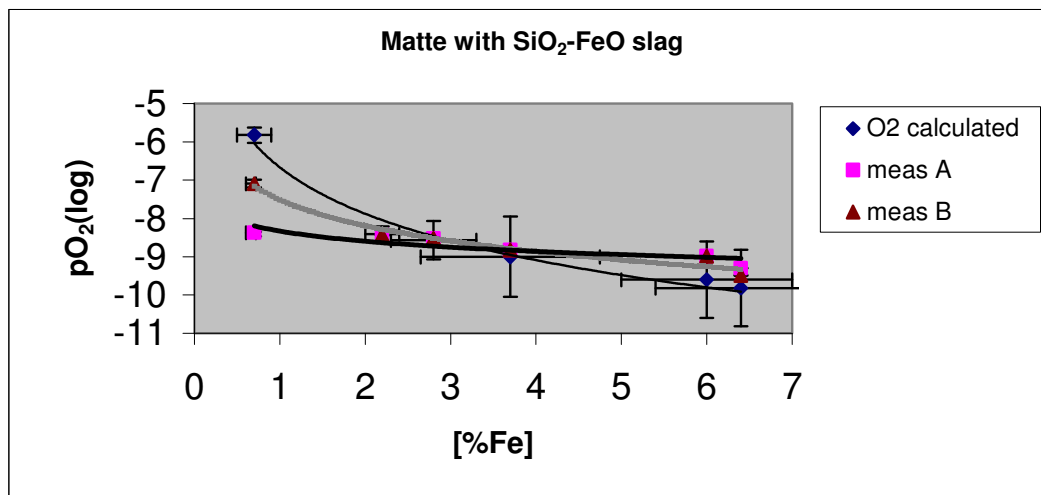


Figure 4-2. Evolution of iron content vs oxygen pressure (FeO slag)

IV.2.2. FeO-Fe₂O₃-SiO₂ slag

The EMF results shown below were obtained using Fe/FeO as reference in Ar atmosphere with FeO-SiO₂-Fe₂O₃ slag. In the figure, 'oxygen calculated' expresses the theoretical calculations (FACTSAGE) to determine the expected oxygen activity.

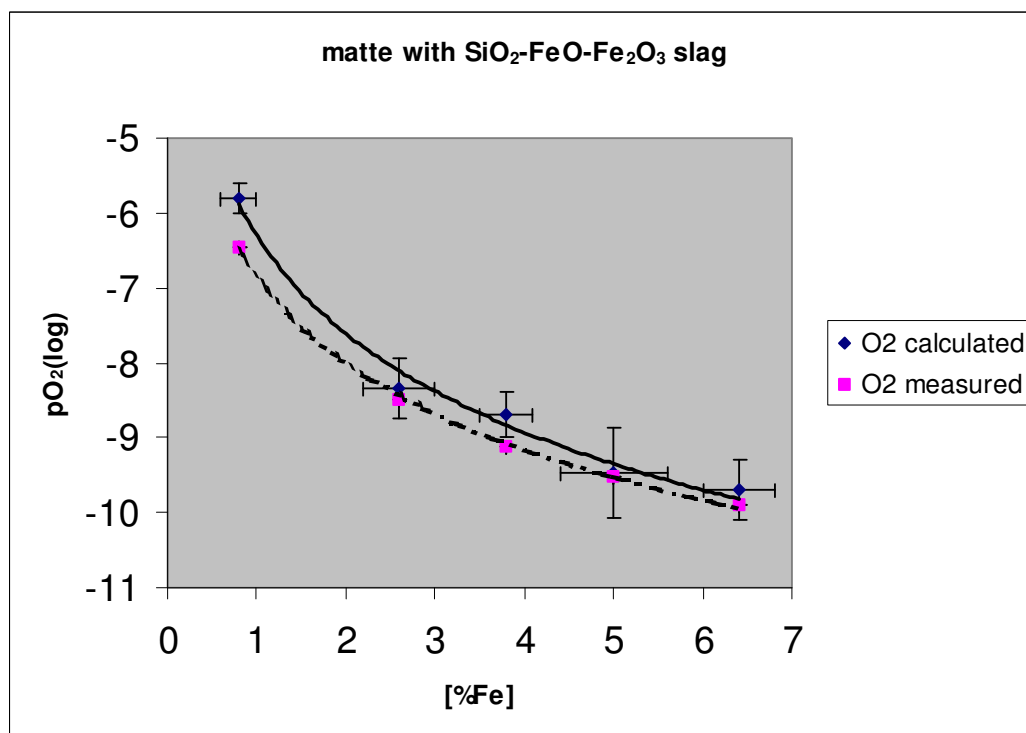


Figure 4-3. Evolution of iron content vs oxygen pressure (FeO/Fe₂O₃ slag)

CHAPTER V.

DISCUSSION OF RESULTS

In this chapter, the results obtained in the previous section (experimental tests) are discussed. The main focus is on the behaviour of oxygen and iron in Fe-Cu-Ni-S matte with two different slag compositions. The first part gives an overview of the results obtained with zirconia probes using Fe-FeO reference electrode. The second part presents the results obtained with the electron probe microanalyser CAMECA SX 100.

V.1. The behaviour of oxygen

The experimental study involved the investigation of the behaviour of oxygen activity for Fe-Cu-Ni-S matte in contact with fayalite slag, as a function of iron content in matte.

1. Figure 4-2 shows the results of the study (values are given in tables B-5 in appendix B). The results plotted on the diagram show the trend of decreasing oxygen activity with increasing matte iron for both results measured. Measurements A differ from measurements B by the sample mass analysed for each test. A high sensitivity is noticed in the average range between 3 and 1 % iron in the matte for both measurements. The different curve shapes are due to the different sample mass, which was larger for series B. The sample mass has an impact on the oxygen activity: with a larger matte volume the measured values approach the predicted values. In series A, the gap between the calculated and measured oxygen partial pressures was much wider. This likely reflects experimental difficulties when working with small samples, rather than any fundamental effect.

This might be due to the better circulation of oxygen between the matte and slag in a bigger volume than smaller one, or simply better contact with the probe by the two phases.

The results obtained with FeO-SiO₂ slag (fig. 4.2) and FeO-SiO₂-Fe₂O₃ slag (fig 4.3) show a similar trend of decreasing oxygen concentrations with increasing iron in the matte. Results for FeO-SiO₂-Fe₂O₃ slags were closer to the expected values compare with those for FeO-SiO₂ slags. This can be because the presence of trivalent iron oxide serves as a better buffer for the

oxygen content of the matte. The results for the $\text{FeO-SiO}_2\text{-Fe}_2\text{O}_3$ are expected to be more representative of actual practical measurements, since converter slags do contain ferric ions.

V.2. Matte analyses.

V.2.1. Tables

All results are tabulated in appendix-H.

V.2.2. Images

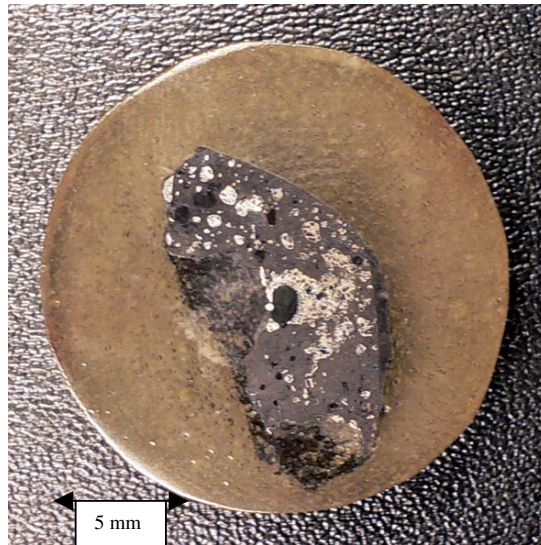
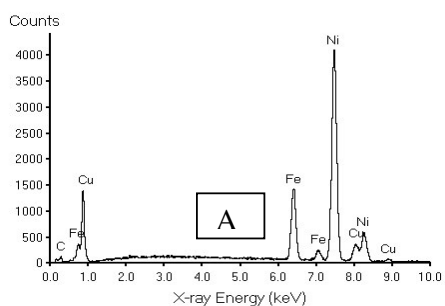
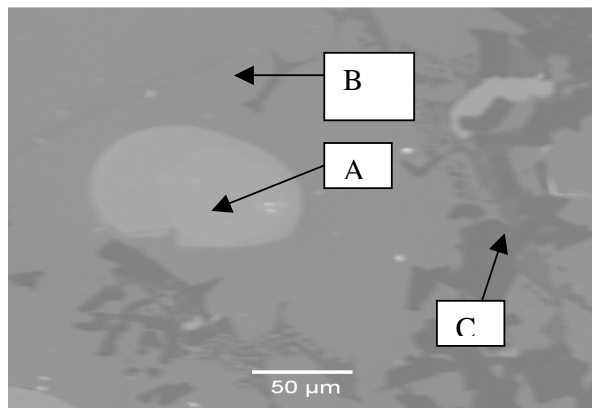
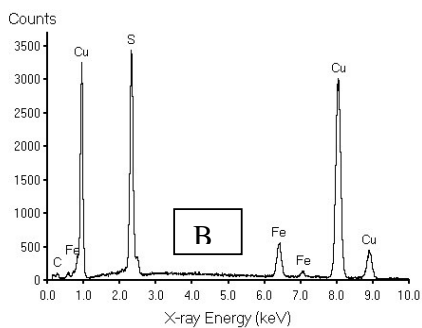


Figure 5-1. Picture of a solidified sample containing sulphide and oxide phases.



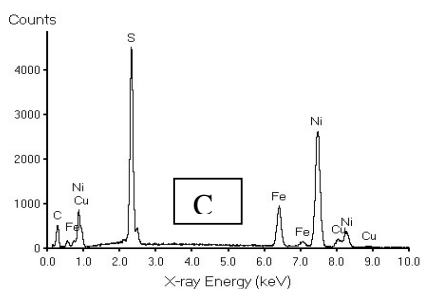
Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (3-Sigma)
Fe-K	0.698	0.97	68.8	67.5	+/- 3.0
Ni-K	0.263	1.04	26.5	27.3	+/- 3.7
Cu-L	0.012	4.38	4.7	5.2	+/- 1.8
S -K	0.000	1.17	0.0	0.0	+/- 0.0
Total			100.0	100.0	

FeNiCu alloy



Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (3-Sigma)
Fe-K	0.007	0.91	0.6	0.6	+/- 0.5
Ni-K	0.005	1.01	0.4	0.5	+/- 0.8
Cu-L	0.630	1.17	59.2	73.8	+/- 3.3
S -K	0.212	1.19	39.9	25.1	+/- 0.6
Total			100.0	100.0	

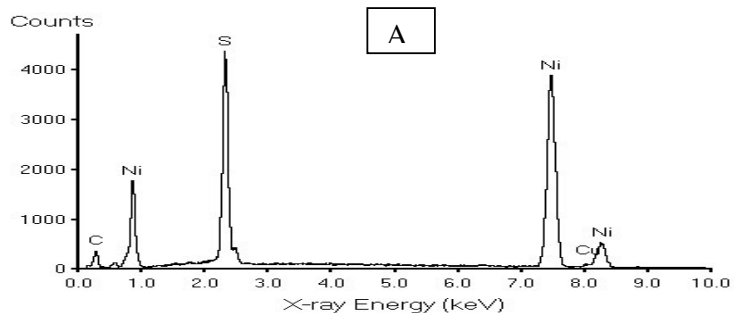
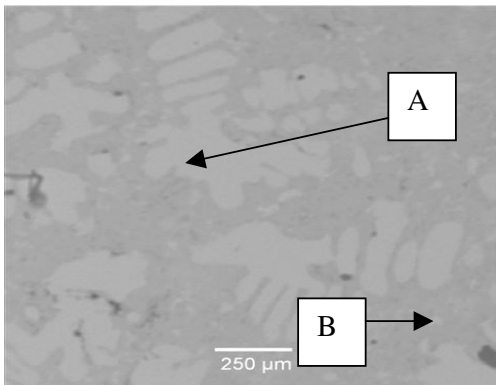
Cu₂S



Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (3-Sigma)
Ni-K	0.670	1.05	57.3	70.0	+/- 1.9
Cu-K	0.021	1.09	1.7	2.3	+/- 0.6
S -K	0.159	1.69	40.3	26.9	+/- 0.7
Fe-K	0.009	0.89	0.7	0.8	+/- 0.3
Total			100.0	100.0	

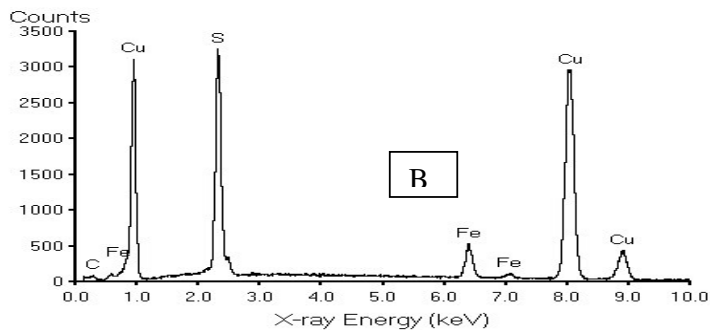
Ni₃S₂

Figure 5.2. Microstructure, EDX and analyses of phases matte in 6.4wt% Fe, 22.8wt%Cu, 48.9wt%Ni and 21.8wt%S



Fe-K	0.004	0.87	0.3	0.4	+/- 0.2
Ni-K	0.690	1.04	59.3	71.8	+/- 1.5
Cu-K	0.023	1.09	1.9	2.5	+/- 0.9
Total			100.0	100.0	

Ni_3S_2



Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (3-Sigma)
S -K	0.129	1.68	35.3	21.7	+/- 0.5
Fe-K	0.058	0.89	4.8	5.2	+/- 0.5
Ni-K	0.001	1.00	0.1	0.1	+/- 0.2
Cu-K	0.691	1.06	59.8	73.0	+/- 1.7
Total			100.0	100.0	

Cu_2S

Figure 5.3. Microstructure, EDX and analyses of phases matte in 6.0wt% Fe, 22.5wt%Cu, 50.7wt%Ni and 21.5wt%S

V.5.3. Comments

As examples, micrographs of two mattes photographed with backscattered mode, EDX spectra and analyses are shown on figure 5-2 and figure 5-3. According to Viljoen[2001:88], the temperature and the bulk composition of a matte determine the path of crystallisation. For the matte represented on figure 5-2 and 5-3, FactSage 5.3.1 calculations between 1250°C and 400°C (temperature where all constituents are supposed solid) shows that the following phases occur depending on the temperature:

1. From 1250°C-750°C: matte
2. At 750°C: Beta_Ni₂S and alloy phases were formed + matte.
3. At 700°C: Cu₂S is formed + alloy stable phase + matte.
4. At 500°C: Ni₃S₂ is formed + Cu₂S + alloy stable phase + Beta_Ni₂S
5. At 450°C: pentlandite is formed + Ni₃S₂+Cu₂S + alloy stable phase.

The matte (liquid) phase decreases and disappears at 600°C. The matte components split into different phases forming heterogeneous sulphide phases.

2. On figure 5-2 and 5-3, the presence of Cu₂S ,Ni₃S₂ and alloy phases is in line with FactSage predictions.
3. Pentlandite expected with FactSage was not present in figure 5-2 and 5-3, probably because cooling took place under non-equilibrium conditions.

However, in general, a good agreement was obtained between results measured and predicted with FactSage.

XRD results presented in Appendix-J show clearly the different major phases, which are in the matte and the slag after the cooling procedure. These major phases agree with those obtained using the SEM results. In the case of the matte, it is heazlewoodite (Ni₃S₂), digenite (Cu₂S) and for the slag, it is fayalite (Fe₂SiO₄) and tridymite (SiO₂).

V.3. Comparison with other investigators.

The relationship between pO₂ and mass% Fe in matte obtained in this thesis seems to be in agreement with the investigation done by Font and *al* [FONT, 1999:16]. They presented a contribution to understanding oxygen blowing of the nickel-copper-iron matte, the phase

equilibrium and the distribution of minor elements such as arsenic and bismuth between the iron-silicate base slag saturated with silica and the $\text{Ni}_3\text{S}_2\text{-Cu}_2\text{S-FeS}$ matte with a Ni: Cu molar ratio of 1. While the initial conditions were different for the two studies, similar conclusions have been found:

Different matte grades were used in the two investigations, different temperatures (1573K with Font and *al* and 1523K in this thesis), different gas composition controlling the system (SO_2 with Font and *al*, SO_2 , CO_2 , CO or Ar with this thesis), different crucibles (magnesia crucible with Font and *al*, silica in this thesis). However, a common decrease of iron content with an increase of oxygen content has been noticed. In Font et *al* investigation, the iron range was from 70mass% Fe in matte to 0mass% Fe in matte, whereas in this thesis the iron range was from 8mass% Fe in matte to 1mass% Fe in matte.

Gisby and *al* [GISBY and al, 2002:26] found the same decreasing trend of iron content for increasing oxygen activity in a general slag-matte-gas system.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The oxygen potential established by contact between Fe-Cu-Ni-S matte and FeO_x-SiO₂ (saturation) slag at 1250°C was investigated. The predicted partial pressure of oxygen varied from 1.53×10^{-8} atm to 2.65×10^{-7} atm for matte. The working temperature was 1250°C, the average temperature used in industry.

The gas composition did not affect the results, therefore the CO-CO₂-SO₂ gas mixture was replaced by Ar for most of the tests. Mattes were sampled using a silica tube, after flushing the furnace with argon. Iron analysis was obtained through the scanning electrode microscope SEM and the electron probe microanalyser. XRD results have been used to verify experiments results. The oxygen partial pressure was calculated and compared with the expected values and it was found to have the same trend for both values.

Two different reference electrodes had been tested. With a Cr/Cr₂O₃ reference, the electromotive force obtained was unstable. Therefore, as alternative a Fe/FeO reference electrode was used showing a stable plateau of EMF for all the results obtained in the laboratory.

Visual examination of the samples after test showed a mixture of different phases containing sulphides, oxides, and alloy.

The oxygen potential was found to increase with decreasing iron content in the matte.

It may be concluded that

- Oxygen is sensitive to iron content below 4% iron content in matte.
- the zirconia probes containing Fe/FeO reference electrode was the better device for oxygen measurements compare with a Cr/Cr₂O₃ reference electrode.
- Gas composition does not affect oxygen activity for measurements performed here.

Zirconia probes can be used to determine the oxygen partial pressure within the furnace at working temperature, to track the iron content in the matte.