BEHAVIOUR OF Cr IN Cu-Fe-Ni-S MATTES

Steven Wright, Sharif Jahanshahi & Shouyi Sun
CSIRO Minerals, Australia

ABSTRACT

The equilibrium distribution of Cr, Cu, Fe and Ni between Cu-Ni-Fe mattes and Pt alloy was measured as functions of the sulphur partial pressure (pS_2), oxygen partial pressure (pO_2), Fe and Cr content of the matte at 1400°C. The distribution ratios of Cr, Cu, Fe and Ni between matte and alloy were independent of oxygen pressure, when the pS_2 was fixed at $2.5x10^{-5}$ atm and pO_2 was varied between 10^{-15} and 10^{-12} atm. The distribution ratio of Cr, Cu, Fe and Ni increased as the sulphur partial pressure increased. For mattes where the proportions of Cu and Ni were kept constant, the distribution ratio of Cr remained constant as the Fe content in the matte increased. The Cr distribution was also found to be independent of the Cr content in the matte, for mattes containing between 2 and 6 wt% Cr.

Cr contents in the Pt alloy were found to be between 0.09 and 0.43 wt%, whereas the concentrations of Fe, Ni and Cu were typically around values of 19-43, 4-12 and 1-3 wt% respectively. The activities of Cr, Cu, Fe, Ni in the matte were calculated using a regular solution model for solid Pt-Fe-Ni-Cu-Cr alloy. The activity coefficient of Cr, Cu, Fe and Ni in the matte decreased as pO_2 and pS_2 increased. The activity coefficients also appeared to be independent of the Fe content. The activity coefficient of Cr was also independent of Cr content in the matte over the concentration range studied. The activity coefficients were extrapolated to evaluate the stability of various oxide and sulphide phases under various conditions.

Key Words: *Activity, Alloy, Matte, Thermodynamics.*

INTRODUCTION

Minor elements in ores and concentrates can have a significant impact on processing and recovery of valuable metals. One element which has a far greater impact than it's concentration in a copper-nickel sulphide concentrate is chromium. The stability of Cr containing spinel phase and the solubility of Cr in the slag formed in the high temperature smelting of Cu-Ni-Fe mattes determines the process operating conditions [2, 11]. As the Cr content in some of the South African ores has been increasing, there has been growing interest in studies on the behaviour of Cr in the slag and how the behaviour changes with fluxing and temperature [1, 2, 10, 11, 15]. The behaviour of Cr in slag is now reasonably well understood, but there has been little published information on the behaviour of Cr in sulphide mattes.

Scanning electron microscopy of quenched samples of industrial Cu-Ni-Fe mattes produced in electric arc furnaces along with the Cr containing slags, identified that Cr was present in the matte in spinel particles and the concentration of Cr dissolved in sulphide grains was close to the detection limit of the Scanning Elecron Microscope Energy Dispersive System (SEM EDS) used to determine the element concentration [18]. Previous work [18, 19] studying the equilibrium distribution of Cu, Ni and Fe between an industrial Cu-Ni-Fe-S matte and Pt alloy, was sufficiently reducing that Cr spinel particles were not observed amongst the matte phase grains. Semi quantitative concentration maps of Cr identified that some Cr had dissolved into both the matte and to a much lesser extent the Pt alloy. As the Cr content in the Pt alloy was less than 0.5 wt% and typically around 0.1 wt%, it's impact on the alloy thermodynamics was neglected. In addition, development work was required to accurately quantify the Cr.

Previously the activity coefficients of Cu, Fe and Ni in the matte were determined from a regular solution model to describe the activities in the solid Pt-Fe-Ni-Cu alloy [18, 19]. The behaviour of Cu, Ni and Fe in the sulphide matte was found to be consistent with the multi-component model developed and experimental data compiled by Kongoli and others. [8] and the work of Somsiri and Gaskell [16] where the same approach was used.

In this paper, the approach of the previous work was extended to Cr with the accuracy of the Cr measurements improved, and to consider the activity behaviour of Cr in the alloy including Pt-Cr [3, 7, 12, 14, Cr-Fe [5, 9], Cr-Ni [5, 9] interactions. Further experiments were performed to examine the effect of Cr content in the matte on the activity coefficient of Cr.

EXPERIMENTAL

The experimental procedure and equipment used has been described in detail in previous papers [18, 19] and was not changed in this study apart from the approach to measure the Cr content in the matte and alloy. Several grams of matte (46% Fe, 11.5% Ni, 8% Cu, 0.26% Cr) was brought into thermal and chemical equilibria with a thin platinum foil under controlled atmospheres of Ar-CO-CO_2-SO_2 at 1400°C. Magnesia crucibles were used as container material and at the end of the equilibration period, the crucible and its content were quenched using water cooling. Polished sections of the matte and Pt alloy were prepared for SEM EDS analysis.

Cr Analysis

In order to check the accuracy of the EDS measurement for Cr, glassy master slags containing between 0.2 and 0.8% Cr_2O_3 were prepared. A master slag of Al_2O_3-CaO-SiO_2 was prepared in a Pt crucible by melting, pouring, quenching, crushing and remelting. To sub-samples of the master slag, Small additions of Cr_2O_3 were added to the master slag, with pouring, quenching, crushing and remelting repeated twice for each addition. After final quenching, glassy pieces were selected and polished for SEM-EDS analysis and sub-samples crushed, and then analysed after wet chemical digestion by ICP-OES. In order to increase the accuracy of the SEM-EDS analysis the data collection period for Cr was increased by 5 times that used for the other elements. This yielded assays for Cr with counting statitsics standard deviations of less than 0.04 wt%. The ICP analysis and the SEM-EDS analysis of the glassy slags are given in Table 1.

Table 1: Comparison of the Cr analysis of a glassy master slag containing various additions of Cr_2O_3 by ICP and SEM-EDS*

Cr_2O_3 addition (wt%)	Cr_2O_3 ICP-OES (wt%)	Cr_2O_3 SEM-EDS (wt%)
0.146%	0.188	0.19 ± 0.02
0.292%	0.294	0.278 ± 0.044
0.438%	0.401	0.409 ± 0.044
0.584%	0.705	0.789 ± 0.044

* SEM analysis of the major components was 18.06 ± 0.08 % Al_2O_3, 39.0 ± 0.1 % CaO, 41.6 ± 0.1 % SiO_2; Average ICP analysis of the major components was 18.3 % Al_2O_3, 37.9% CaO, 41.92% SiO_2

Time to Approach Equilibrium for Cr

The time required to approach equilibrium with respect to Cu, Fe and Ni was presented in the previous work. The time was determined by establishing when the composition of the platinum was uniform across the thickness of the foil and the compositions of the alloy and matte did not vary with reaction time. The experiments were performed at 1400°C at a oxygen partial pressure (pO_2) of 10^{-9} atm and sulphur partial pressure (pS_2) of 8 $x10^{-3}$ atm, with reaction times between 8 and 72 hours. By 49 hours, the composition of the platinum foil and fine droplets in the matte were uniform across their thickness and there were no compositional differences with respect to Cu, Fe and Ni when compared with the foil equilibrated for 72 hours [18, 19]. The variation of the distribution ratio of Cr, Cu, Fe and Ni is shown in Figure 1. Cr has also attained equilibrium after 30 hours, the scatter in the distribution ratio can be attributed to the low Cr content in the alloy, between 0.01 and 0.02 wt%. Thus matte and alloy had attained an equilibrium Cr distribution after 49 hours, which was the reaction period used for the remainder of the study.

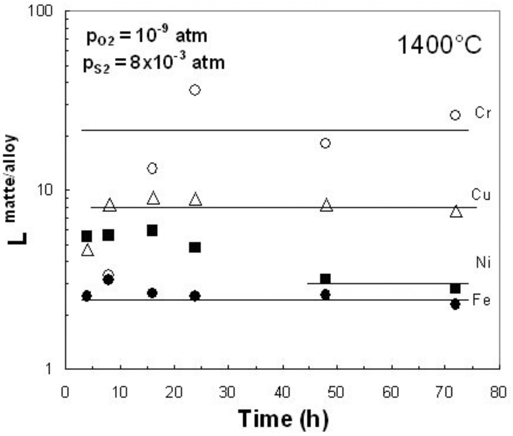

Figure 1: Distribution ratio of Cr, Cu, Fe and Ni with time for experiments performed at 1400°C under a pO_2 of 10^{-9} atm and pS_2 of 8×10^{-3} atm

RESULTS

The matte used in this work was an industrial matte and contained Cr as a chrome spinel. More reducing conditions ($pO_2 = 10^{-12}$ to 10^{-15} atm) were used to destabilise Cr spinel. Under the more reducing conditions, Cr associated in the quenched matte with Fe and S, forming a (Fe,Cr)S solid solution. Figure 2 shows the back-scattered electron image (BSE) and the EDS chemical maps of a section of quenched matte, showing that Cr does not associate with the Cu and Ni containing phases, but mainly with Fe and S.

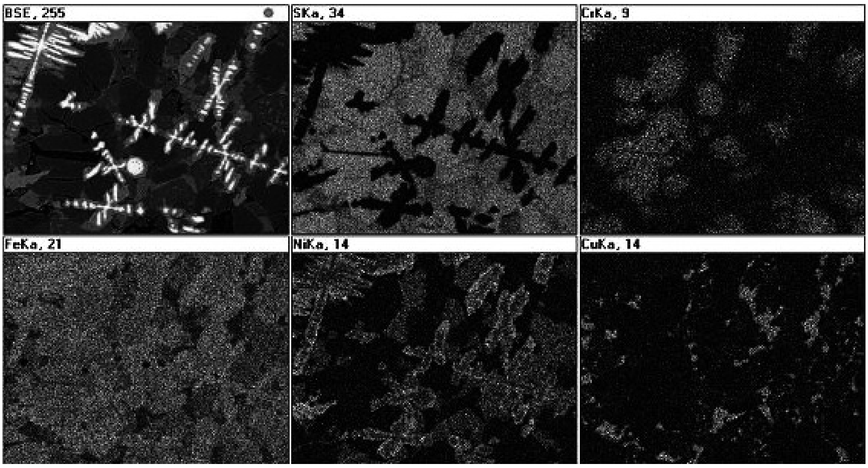

Figure 2: Backscatter electron image and EDS chemical maps showing the distribution of S, Cr, Fe, Ni and Cu in quenched matte. The brighter or greater the contrast, highlights element concentration and concentration differences in phases. The bright phase in the BSE image is the Pt rich metal phase

The effect of Cr content in the matte at a pS_2 of 2.5×10^{-5} atm and pO_2 of 10^{-15} atm at 1400°C on the distribution ratio of Cu, Fe and Ni is shown in Figure 3. Small additions of Cr metal were added to crucible containing the matte and platinum prior to equilibration. Considering the The distribution ratios of Cr, Cu, Fe and Ni do not vary over the Cr composition range of 2.4 to 6 wt%.

The distribution ratio for Cr, Cu, Fe and Ni between the matte and alloy ($L_{matte/alloy}$) at 1400°C where the sulphur partial pressure was fixed at 2.5x10^{-5} atm and the oxygen partial pressure varied between 10^{-15} and 10^{-12} atm is shown in Figure 4. The distribution ratios of the metals remained constant and did not vary with pO_2. When the pO_2 was fixed at 8x10^{-13} atm and the sulphur partial pressure varied between 2x10^{-5} to 5x10^{-3} atm. (Figure 5), the $L_{matte/alloy}$ for Cr, Cu, Fe and Ni increased as the pS_2 increased.

The effect that changing matte chemistry may have on the distribution of Cr, Cu, Fe and Ni is shown in Figure 6, where the distribution ratio is plotted against the Fe content in the matte. The Cr distribution is scattered around a value of 15 as the iron content in the matte varied between 37 and 52 wt%. The Fe and Ni distributions do not change significantly as the matte chemistry changes, but the Cu distribution increased as the Fe concentration increased.

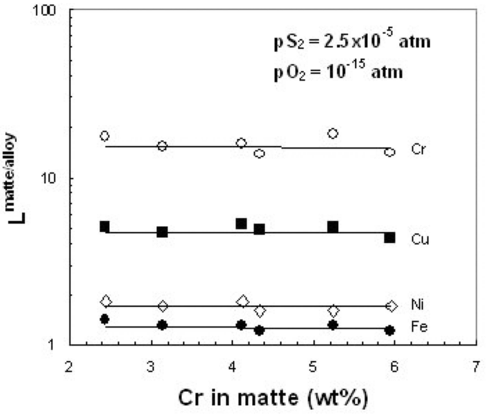

Figure 3: Variation of equilibrium distribution of Cr, Cu, Fe and Ni between matte and Pt-alloy ($L^{matte/alloy}$) with the Cr content of the matte at $p0_2$ of 10^{-15} atm and pS_2 of 2.5x10^{-5} atm at 1400°C

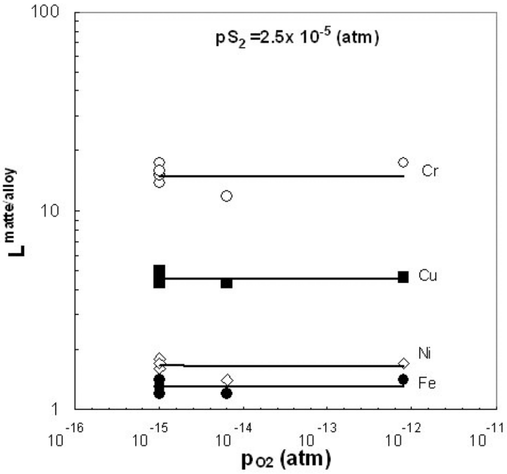

Figure 4: Distribution of Cr, Cu, Fe and Ni between matte (45% Fe, 11% Ni, 8% Cu, 3% Cr) and alloy at 1400°C at a fixed sulphur partial pressure as a function of oxygen partial pressure

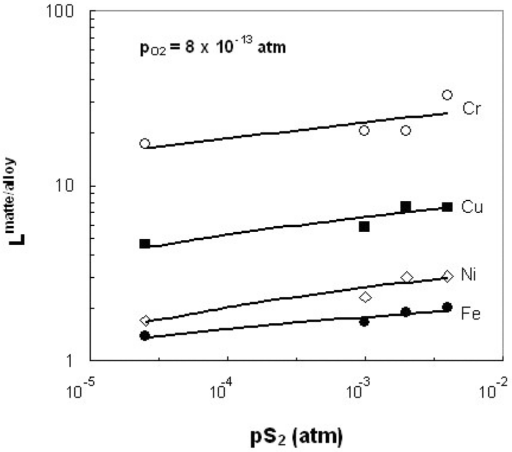

Figure 5: Distribution of Cr, Cu, Fe and Ni between matte (45% Fe, 11% Ni, 8% Cu, 3% Cr) and alloy at 1400°C; at an oxygen partial pressure of $8x10^{-13}$ atm, as a function of sulphur partial pressure

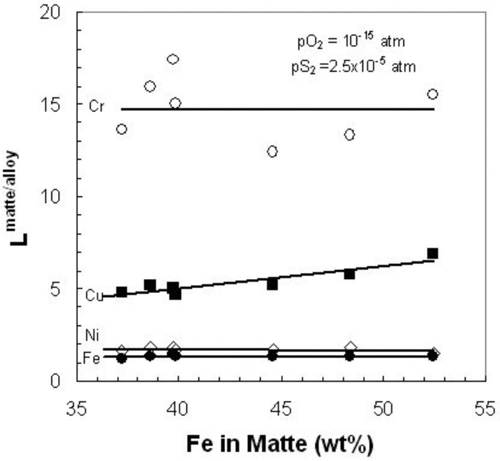

Figure 6: Effect of Fe content in the matte on the Cr, Cu, Fe and Ni distribution at pO_2 of 10^{-15} atm and pS_2 of $2.5x10^{-5}$ atm at 1400°C

DISCUSSION

The thermodynamic behaviour of Cu, Fe and Ni in the mattes has been discussed in detail previously and the results compared with other published studies [18, 19]. Although there were no previous studies performed under the same conditions, the trends observed with respect to pO_2, pS_2, matte chemistry were consistent with studies on comparable matte chemistry. It was found that the activity of Cu and Ni in these mattes shows positive departure from ideal behaviour, while Fe shows negative deviation. The discussion here examines the behaviour of Cr in these mattes.

The regular solution model developed previously for Pt alloys [19] has been expanded to include the interaction parameters for Cr taken from published activity data [3, 5, 7, 9, 12, 14]. The activity coefficients (γ) in the matte were calculated from the activities of Cr, Cu, Fe and Ni in the alloy. The standard state for Cu being pure liquid, with Cr, Fe and Ni being pure solid.

The activity coefficient of Cr in the matte was found to be independent of chrome content over the concentration range examined. The distribution ratio for Cr was in favour of the matte with a value of 15. The concentration of Cr in the metal was in the range of 0.14 to 0.43 wt% and the activity coefficient of Cr in the metal was in a linear region with respect to concentration. Therefore γ_{Cr} in the matte was constant with a value of 0.090. Table 2 shows the calculated activity of Cr_2O_3 and Cr_3O_4 using thermochemical data [13, 17]. At an oxygen potential of 10^{-15} atm, the activity of Cr_2O_3(s) in the matte ranged between $6.9x10^{-7}$ and $4.3x10^{-6}$ for the concentration range of 2-6 wt% studied, indicating it was not likely to be stable. Cr_3O_4 was predicted to be even less stable. Cr was unlikley to be in a solid solution with other spinels. The matte phase was also not saturated with CrS, as the calculated activity of CrS was between $2.2x10^{-2}$ and $5.7x10^{-2}$. The presence of a (Fe,Cr)S solid solution in the quenched matte was due to the ease at which the phases crystallise from the liquid matte on cooling to room temperature.

Figure 7 shows that at fixed sulphur partial pressure, γ_{Cr}, γ_{Cu} and γ_{Fe} decrease with increasing oxygen partial pressure and γ_{Ni} appears to remain constant over the oxygen partial pressure range studied. Figure 8 shows that the activity coefficients of Cu, Fe and Ni decrease with increasing sulphur partial pressure. The activity coefficient of Cr has scattered values at the higher sulphur partial pressure (with a possible contribution from the low level of Cr observed in the alloy (cf 0.09 wt%) for one experiment, however considering the behaviour of the activity coefficient Fe and Ni with sulphur partial pressure, consistent behaviour of Cr with respect to these elements is expected.

The effect of Fe content in the matte on the activity coefficients of Cr, Cu, Fe and Ni from this study are shown in Figure 9. At fixed oxygen and sulphur pressures the activity coefficients do not vary with Fe content in the matte over the composition range examined.
A least squares regression of the 1400°C Cr activity coefficient data, yields the following relationship for the activity coefficient in the matte: $\gamma Cr = -0.105 - 0.00447 \ln (pO_2) - 0.00385 \ln (p_{S2})$ Valid: p_{O2} between 10^{-15} and 10^{-9} ; pS_2 10^{-5} and 10^{-2}.

Matte-Spinel Equilibrium

As presented above, the time series of experiments were performed at a higher oxygen and sulphur partial pressures than the rest of the study. The Cr content in the matte and alloy were close to the limit of detection of the SEM-EDS system. A few chrome containing spinel crystals were found in the time series experiments and the crystals were near the crucible/matte interface. The spinel crystals had an average Mg/Fe atomic ratio of 1.2 with the Cr/(Mg+Cr ratio of 1.6. This stoichiometry approximates to a mixture of $MgCr_2O_4$, $FeCr_2O_4$ and $MgFe_2O_4$, with respective mole fractions of 0.56, 0.36 and 0.08.

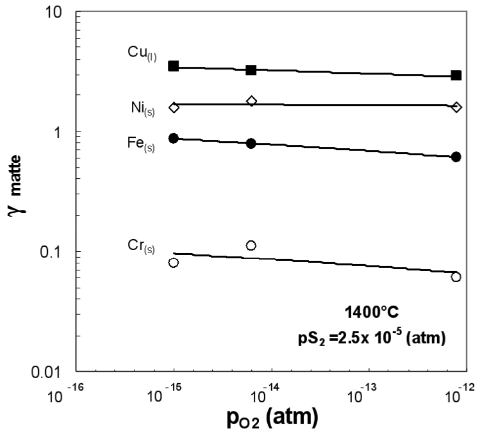

Figure 7: Effect of oxygen partial pressure on the activity coefficient of Cr, Cu, Fe and Ni in matte containing 45% Fe, 11% Ni, 8% Cu, 3% Cr at fixed sulphur partial pressure of 2.5x10^{-5} atm and 1400°C

For a matte equilibrated at a pO_2 of 10^{-15} atm and pS_2 of 2.5x10^{-5} atm, γ_{Cr} has a value of 0.086. Under the conditions of the time to approach equilibrium series; pO_2 of 10^{-9} atm and pS_2 of 7.9x10^{-3} atm, γ_{Cr} in the matte has a value of 0.006. The average Cr content in the matte at equilibrium was 0.2 wt% (i.e., x_{Cr} = 0.002). The calculated activity of solid chrome oxide (Cr_2O_3) was 0.035 and the activity of the thermodynamically unstable chrome spinel (Cr_3O_4) was 5.3x10^{-5}. The Cr content in the metal was too low to determine accurately, but γ_{Cr} in the matte can be estimated from the above equation.

Table 2: Calculated activites of Cr species or spinels in equilibrium with matte at 1400°C under a pO_2 of 10^{-15} atm or 10^{-9} atm

Reaction	K_R (1400°C)	pO_2 (atm)	pS_2 (atm)	γ_{Cr} (matte)	x_{Cr} (matte)	a_{Fe}	a_{MgO}	Specie	Activity
$2\,Cr_{(s)} + 3/2\,O_2(g) = Cr_2O_{3(s)}$	6.7x10^{21}	10^{-15}	2.5x10^{-5}	0.086	0.02			a_{Cr2O3}	6.9x10^{-7}
		10^{-15}	2.5x10^{-5}	0.086	0.05				4.3x10^{-6}
$3\,Cr_{(s)} + 2\,O_2(g) = Cr_3O_4(s)$	3.08x10^{28}	10^{-15}	2.5x10^{-5}	0.086	0.02			a_{Cr3O4}	1.8x10^{-10}
	3.08x10^{28}	10^{-15}	2.5x10^{-5}	0.086	0.05				2.8x10^{-9}
$Cr(s) + ½\,S_2(g) = CrS_{(s)}$	2.5x10^{3}	10^{-15}	2.5x10^{-5}	0.086	0.02			a_{CrS}	0.022
	2.5x10^{3}	10^{-15}	2.5x10^{-5}	0.086	0.05				0.057
$2\,Cr_{(s)} + 3/2\,O_2(g) = Cr_2O_3(s)$	6.7x10^{21}	10^{-9}	7.9x10^{-5}	0.006	0.002			a_{Cr2O3}	0.035
$3\,Cr(s) + 2\,O_2(g) = Cr_3O_4(s)$	3.08x10^{28}	10^{-9}	2.5x10-5	0.006	0.002			a_{Cr3O4}	5.3x10^{-5}
$Cr(s) + ½\,S_2(g) = CrS(s)$	2.5x10^{3}	10^{-9}	7.9x10^{-3}	0.006	0.002			a_{CrS}	0.067
$Fe_{(s)} + 2\,Cr_{(s)} + 2O_2(g) = FeCr_2O_{4(s)}$	1.24x10^{28}	10^{-9}	7.9x10^{-3}	0.006	0.002	0.067		$a_{FeCr2O4}$	0.135
$MgO_{(s)} + Cr_2O_{3(s)} = MgCr_2O_{4(s)}$	14.22	10^{-9}	7.9x10^{-3}	0.006	0.002		1	$a_{MgCr2O4}$	0.50
$MgO_{(s)} + 2\,Fe_{(s)} + 3/2\,O_{2(g)} = MgFe_2O_{4(s)}$	2.8x10^{12}	10-9	7.9x10^{-3}	0.006	0.002	0.067	1	$a_{MgFe2O4}$	0.0004

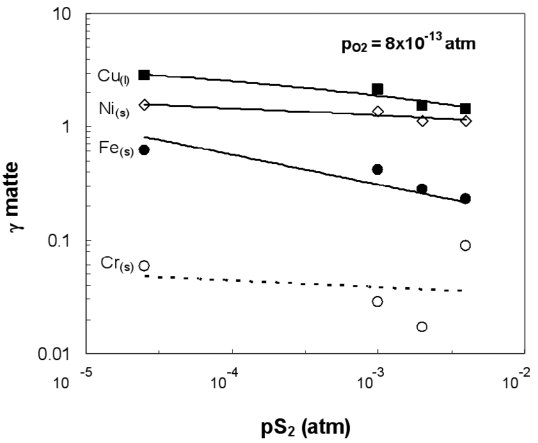

Figure 8: Effect of sulphur partial pressure on the activity coefficient of Cr, Cu,Fe and Ni in matte containing 45% Fe, 11% Ni, 8% Cu, at fixed oxygen partial pressure of $8x10^{-13}$ atm and 1400°C

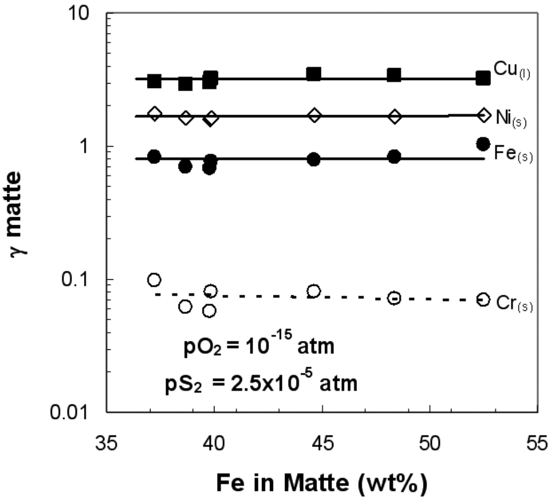

Figure 9: Effect of iron content in the matte on the activity coefficient of Cr, Cu, Fe and Ni in Cu-Fe-Ni-S mattes at 1400°C at $p0_2 = 10^{-15}$ and $pS_2 = 2.5x10^{-5}$ atm

Using the free energy of various reactions [13, 17] to form spinel phases/components, the activity of the spinel components can be determined. The calculated activities are given in Table 2. The activity of $FeCr_2O_4$ was calculated from the free energy of formation from the elements, using the activity of Fe in the alloy (0.067), the concentration of Cr and the calculated activity coefficient of Cr in the matte and the equilibrating oxygen partial pressure. The activity of *solid* $FeCr_2O_4$ was calculated to be 0.135. The activity of $MgCr_2O_4$ can also be calculated from the free energy of formation from the oxides [13] assuming the spinel was in equilibrium with the MgO crucible containing the matte and alloy. The calculated $MgCr_2O_4$ activity was 0.5. Similarly, the activity of $MgFe_2O_4$ was calculated to be $4.0x10^{-4}$. The available thermodynamic data for the binary $MgCr_2O_4$-$FeCr_2O_4$ [4, 6] spinel show that there is a slight negative departure from ideal behaviour and similar behaviour is expected in the ternary spinel. Based on the composition of the spinel above, the activity coefficients of $MgCr_2O_4$, $FeCr_2O_4$ and $MgFe_2O_4$ were 0.89, 0.375 and 0.005 respectively. If the system is considered as a binary, there is relatively good agreement of the calculated spinel component activities with the published data considering the extrapolation of the activity coefficient of Cr in the matte to the higher oxygen and sulphur partial pressures and considering the accuracy of determining the Cr content in the matte.

CONCLUSIONS

The equilibrium distribution of Cr, Cu, Fe and Ni in Cu-Fe-Ni mattes and solid Pt alloys was studied at 1400°C. For a matte containing 45% Fe, 11% Ni, 8% Cu, at 1400°C, the following behaviour was observed for the distribution ratios of Cr, Cu, Fe and Ni:

- For mattes where the proportions of Cu, Fe and Ni were kept constant and the Cr content varied between 2 and 6 percent, the distribution ratio of Cr ($L^{matte/alloy}$) was constant with a value of 15.
- Under the range of sulphur and oxygen pressures of this study where $pS_2 = 2.5x10^{-5}$ atm and pO_2 was between 10^{-15} and 10^{-12} atm, the distribution ratios of Cr, Cu, Fe and Ni between matte and alloy were virtually independent of oxygen pressure and had values of 15, 4.5, 1.6 and 1.2 respectively.
- The distribution ratio of Cr, Cu, Fe and Ni increased as the sulphur partial pressure increased. At a pO_2 of $8x10^{-13}$ atm, the distribution ratios had increased from the above values to 25, 7.8, 2.1 and 3 respectively when $pS_2 = 8x10^{-3}$ atm.
- For mattes where the proportions of Cu and Ni were kept constant, the distribution ratio of Cu increased as the Fe content in the matte increased. The Cr, Fe and Ni distribution appeared to be independent of the iron content in the matte and had a value of 15, 1.2 and 1.6 respectively.

The activity coefficient of Cr in the matte behaved in the following manner:

- For mattes with a constant ratio of Cu/Fe/Ni, γ_{Cr} was independent of the chromium content of the matte. For mattes where the ratio of Cu to Ni was constant at 0.6, γ_{Cr} was also independent of the iron content. γ_{Cr} had a value of 0.086 at a pO_2 of 10^{-15} atm and pS_2 of $2.5x10^{-5}$ atm.
- At fixed sulphur partial pressure, γ_{Cr} decreased with increasing pO_2. γ_{Cr} had a value of 0.086 at a pO_2 of 10^{-15} atm and 0.056 at a pO_2 of 10^{-12} atm.
- At fixed oxygen partial pressure, γ_{Cr} decreased as the sulphur partial pressure increased following the behaviour observed for Cu, Fe and Ni. At a pO_2 of $8x10^{-13}$ atm and pS_2 ranging from $2.5x10^{-5}$ to $4x10^{-3}$ atm, γ_{Cr} decreased from a value of 0.056 to 0.038.

The behaviour of the activity coefficient of Cr in the matte was consistent with the behaviour of the activity coefficients of Fe and Ni in the matte.

Extrapolation of the activity coefficient for Cr in the matte to higher oxygen and sulphur partial pressure yielded calculated activities close to that expected for spinels in equilibrium with the matte phase.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support for this work by CSIRO Minerals, Anglo Platinum, Impala Platinum and Lonmin Platinum through AMIRA International.

REFERENCES

Bartie, N., Eksteen, J., Jahanshahi, S. & Sun, S. (2003). *Proceedings of the XXII International Minerals Processing Congress*. Cape Town, South Africa. [1]

Eric, R. H. (2004). *7th International Conference on Molten Slags, Fluxes and Salts*. Cape Town, South Africa, pp.531-541, SAIMM, Johannesburg. [2]

Garbers-Craig, A. & Dippenaar, R. (1997). *Metal. Mater. Trans. B*. Vol. 28, pp. 547-552. [3]

Hino, M., Higuchi, K., Nagasaka, T. & Ban-ya, S. (1994). *ISIJ Int.* Vol. 34, pp. 739-45. [4]

Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M. & Kelley, K. K. (1973). *Selected Values of the Thermodynamic Properties of Binary Alloys*. Amer. Soc. Met., Metals Park, Ohio. [5]

Jacob, K. T. & Iyengar, G. N. K. (1999). Metall. Mater. Trans. B, Vol. 30, pp. 865-71. [6]

Kay, D. A. R. & Mohanty, A. K. (1970). Metallurgical Transactions, 1970, Vol. 1, pp. 303-304. [7]

Kongoli, F., Dessureault, Y. & Pelton, A. D. (1998). Metall. Mater. Trans. B, Vol. 29, pp. 591-601. [8]

Lister, P. C. & Bell, H. B. (1969). Trans. Met.Soc. AIME, Vol. 245, pp. 2273-2277. [9]

Morita, K. & Sano, N. (2004). 7th International Conference on Molten Slags, Fluxes and Salts, Cape Town, South Africa, pp. 113-117, SAIMM, Johannesburg. [10]

Nell, J. (2004). 7th International Conference on Molten slags, Fluxes and Salts, Cape Town, South Africa, pp.165-170, SAIMM, Johannesburg. [11]

Pretorius, E. B. & Muan, A. (1992). J. Amer. Ceram. Soc., Vol. 75, pp. 1361-1363. [12]

Robie, R. A., Hemingway, B. S. & Fisher, J. R. (1979). *Thermodynamic Properties of Minerals and Related Substances at 298,15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures*. US Geological Survey, Washington. [13]

Schwerdtfeger, K. & Muan, A. (1965). Trans. Met. Soc. AIME, Vol. 233, pp. 1904-1906. [14]

Somerville, M., Wright, S., Sun, S. & Jahanshahi, S. (2004).7th International Conference on Molten slags, Fluxes and Salts, Cape Town, South Africa, pp. 219-224, SAIMM, Johannesburg. [15]

Somsiri, C. & Gaskell, D. R. (1995). Metall. Mater. Trans B, Vol. 26, pp. 1157-1164. [16]

Toker, N. Y., Darken, L. S. & Muan, A. (1991). Metallurgical Transactions B, Vol. 22, pp. 225-232. [17]

Wright, S., Jahanshahi, S. & Sun, S. (2003). Proceedings of the XXII International Minerals Processing Congress, Cape Town, South Africa. [18]

Wright, S., Jahanshahi, S. & Sun, S. (2005). *Mineral Processing and Extractive Metallurgy.* (Trans IMM Section C), Vol. 114, No. 3, 2005, pp. C147-C153. [19]