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Activities of Cu, Fe and Ni in Cu-Fe-Ni-S mattes

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The equilibrium distribution of 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), temperature and Fe content of the matte. The distribution ratios of 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 Cu, Fe and Ni increased as the sulphur partial pressure increased. The Cu and Ni distribution ratios decreased with increasing temperature and the Fe distribution ratio increased slightly over the temperature range of 1350–1500°C. 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 Fe and Ni distribution appeared to be independent of the iron content in the matte and had a value of 1.2 and 1.6 respectively.

The activity of Cu, Fe, Ni in the matte was calculated using a regular solution model for solid Pt-Fe-Ni-Cu alloy. The activity coefficient of Cu, Fe and Ni decreased as pO_2 and pS_2 increased. The activity coefficients also appeared to be independent of the Fe content and temperature over the range of 36 to 54 wt% iron and 1350 to 1500°C respectively.

Keywords: activity, alloy, matte, thermodynamics

Introduction

Knowledge of the thermodynamic behaviour of mattes is a key component in improving and developing non-ferrous smelting processes. In developing a thermodynamic model of Fe-Ni-Cu-Co-S mattes, Kongoli and colleagues[1] reviewed the available data on the binary systems, Ni-S, Fe-S, Cu-S, Co-S and ternary Fe-Ni-S, Cu-Ni-S, Cu-Fe-S, for which there was an extensive reference list. Only one higher order system was examined: the Cu-Fe-Ni-S system, for which there had been only 2 previous studies[2,3]. These studies concentrated on the variation of sulphur content in the matte at fixed sulphur partial pressure activity with Fe and Ni content, and the activity-composition data of other components in the Cu-Fe-Ni-S matte could not be accurately determinable.

Various experimental techniques have been developed that allow the thermodynamic description of binary and ternary mattes to be determined. One extensively used technique is gas-matte equilibration where the matte is equilibrated at controlled sulphur partial pressure with H_2/H_2S gas mixtures and then the activity of the metal components are determined by Gibbs-Duhem integration. Another approach to determine activities of species in mattes and slags is to use an alloy phase as a 'probe' that can be used to measure thermodynamic behaviour of multicomponent melts. The present study is an extension of the technique used by Somsiri and Gaskell where the gas phase sulphur and oxygen partial pressures are controlled and the activity of Cu and Fe were determined by equilibrating a Pt foil with the matte[4]. The activity of Cu and Fe in the matte was determined from knowledge of the thermodynamics of the solid Pt alloy.

This paper presents the results of a study where the thermodynamics of the industrial matte (furnace matte) containing copper, iron and nickel was measured by equilibrating the matte with platinum. Using the established data on the activity of Cu[5-7], Fe[8-13] and Ni[14-16] in Pt alloys and the thermodynamics of solid Cu-Fe[7], Ni-Fe[17-20], and Cu-Ni[17,18,20] alloys a regular solution model for the Pt alloy can be used to calculate the activities of Cu, Fe and Ni in the matte as well as knowing the sulphur and oxygen fugacities.

Experimental

Equipment

Equilibration experiments were performed in a sealed vertical tube furnace. A molybdenum disilicide heating element furnace was used to provide external heat to the work tube. With the work tube in place, the furnace provided a region of constant temperature (within ±2°C) about 50 mm long, located close to the middle of the furnace.

Figure 1 shows the schematic of the suspended crucible in the work tube. The work tube had an inner diameter of 50 mm and was fitted with water-cooled brass end caps. A seal between the end caps and the ceramic work tube was achieved by rubber o-rings. A snug fitting brass plug and bottom plate capped the end caps. O-rings were also used to provide seals between metal and ceramic components including the crucible support, and the tube from which the crucible was suspended.

The crucible support consisted of castable refractory platform 40 mm diameter and 15 mm thick and was cast onto an alumina tube. An 'R' type thermocouple fitted inside the alumina tube and measured the temperature at the top of the ceramic platform. The ceramic platform was positioned in the hot zone so that it was in the uniform temperature region of the furnace.

An eggcup sized and shaped magnesia crucible (15 mm ID at base, 46 mm high with a 33 mm ID at the top) was suspended from an alumina tube (8 mm OD, 5 mm ID) by a 3mm diameter alumina rod, which passed through 3 mm diameter holes in the alumina tube and the crucible. A ceramic heat shield with a 10 mm diameter central hole fitted over the lance and covered the crucible. A small quantity of refractory cement was applied to secure the crucible, alumina pin and heat shield in position.

The gas mixture used to fix the sulphur and oxygen partial pressure of the experiment was introduced at the bottom of the furnace, and exited the furnace by passing through spaces between the heat shield and the crucible and then out of the furnace via the alumina tube. A bubbler connected to the alumina tube by flexible tubing was used to prevent air ingress. Electronic gas mass flow controllers controlled the flow rates of carbon monoxide, carbon dioxide and 1% or 15% sulphur dioxide in nitrogen. The flow rates of the gases were also calibrated using the soap film displacement method. The gas flow rate was 5 $cm^3\ s^{-1}$

Materials

An industrial matte was used in this study as a starting material. The 'as received' matte sample was dried at 105°C and then crushed to a particle size passing a 2 mm screen (approximately) and then stored in a glass jar. The composition of the matte was 9.4% Cu, 38.6% Fe, 17.4% Ni and 29% S. Technical grade iron sulphide was used to alter the Fe content of the matte.

Platinum foil of 150µm thickness was used to equilibrate with the matte. The foil was cut into squares of approximately 10 mm x 12 mm dimensions with a mass of 0.4 g. To compensate for iron loss to the platinum, iron foil with a thickness of 100 µm and 99.5% purity was also used. The iron foil was cut into pieces of similar dimensions to the Pt foil and had a mass of 0.17 g.

The gases used to fix the sulphur and oxygen partial pressure were chemically pure grade carbon monoxide, food grade carbon dioxide, and mixtures of sulphur dioxide in nitrogen supplied with certificates of analysis. Two mixtures of sulphur dioxide in nitrogen were used, 14.4±0.2% and 1.05±0.05%. The gases were passed through driers filled with magnesium perchlorate to remove trace levels of moisture and 'oxygen getter' furnaces to remove trace levels of oxygen.

Procedure

The following procedure was adopted to conduct the equilibrium experiments between the matte, alloy and gas phases.

The Pt foil was added to a magnesia crucible along with a weighed piece of Fe foil. Five grammes of matte was then weighed into the crucible. The crucible was suspended and cemented to the alumina tube and covered with a ceramic heat shield. The brass plug was lowered over the alumina tube until just above the crucible.

The brass plug (and crucible) was then located in the top end cap and the crucible was kept up high in the furnace in the cold zone. The tube furnace, which was at a temperature of 800°C, was then purged with nitrogen for 15 minutes, and then the equilibrating gas mixture was introduced into the furnace. After a further 10 minutes, the crucible was lowered into the hot zone. The furnace temperature was then increased to the desired equilibration temperature. The crucible remained in place for a set reaction/equilibration period, and was then rapidly removed from the furnace and quenched in water.

After quenching, the crucible was dried in air and was mounted in resin. The crucible was vertically sectioned to reveal a slice of matte and the Pt alloy. The slice was polished, carbon coated and the composition of the alloy and matte phases determined using a quantitative EDS system on a scanning electron microscope (SEM).

Time to approach equilibrium

The time required to approach equilibrium 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. Experiments were performed at 1400°C at an oxygen partial pressure (pO_2) of 10^{-9} atm and sulphur partial pressure (pS_2) of 8 $x10^{-3}$ atm, at reaction times of 8, 16, 24, 49 and 72 hours. The composition of the matte was determined by analysing over several large areas free of Pt (minimum dimensions (50µm x 50µm). The sulphur analysis of the matte suggested that the gas/matte equilibrium was established reasonably quickly as the sulphur content of the matte remained constant after 8 hours reaction time. The composition of the platinum was determined by point analysis at several micron steps across the foil thickness. As the reaction time progressed, the platinum foil increased in thickness due to diffusion of Fe, Ni and Cu into it[21]. After a reaction time of 49 hours, the width of the foil was no longer uniform, and fingers on the foil and large droplets of platinum alloy were observed. The composition of the foil and the droplets was uniform across the foil thickness and there were no compositional differences when compared with the foil equilibrated for 72 hours[21]. Thus a reaction time of 49 hours was chosen for the remainder of the study.

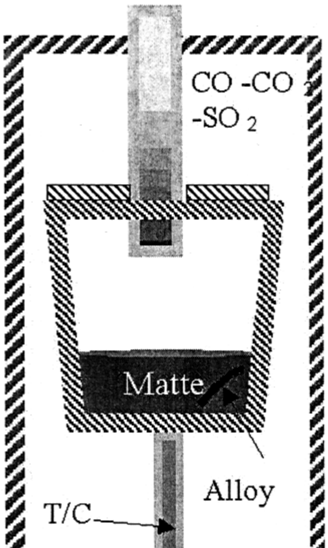

Figure 1. Schematic of the suspended crucible inside the work tube

Table I
Experimental conditions and composition of matte and Pt alloy

		Gas		Matte					Alloy		
No.	Temp (°C)	pO_2 (atm)	pS_2 (atm)	Cu (wt%)	Fe (wt%)	Ni (wt%)	S (wt%)	O, Pt & Impurities (wt%)	Fe (wt%)	Ni (wt%)	Cu (wt%)
Varying pO_2, fixed pS_2 and temperature											
1	1400	7.9 x10^{-13}	2.5 x10^{-5}	9.40	40.67	15.91	26.47	7.56	29.84	9.50	2.10
2	1400	6.3 x10^{-15}	2.5 x10^{-5}	9.88	39.54	14.87	27.37	8.34	33.16	10.75	2.36
3	1400	1.0 x10^{-15}	2.5 x10^{-5}	8.60	38.18	14.39	29.3	9.51	33.41	8.48	2.03
4	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.29	38.96	15.27	26.44	10.1	31.67	8.73	1.84
5	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.41	39.76	15.63	26.74	8.29	30.22	8.73	1.96
6	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.74	39.85	15.72	25.84	8.58	31.93	9.66	2.17
Varying pS_2, fixed pO_2 and temperature											
7	1400	7.9 x10^{-13}	4.0 x10^{-3}	9.28	37.95	15.86	29.35	7.57	19.60	5.37	1.27
8	1400	7.9 x10^{-13}	2.0 x10^{-3}	8.76	39.52	15.68	29.39	6.66	21.48	5.34	1.18
9	1400	7.9 x10^{-13}	1.0 x10^{-3}	8.87	39.98	15.58	28.15	7.43	24.90	6.97	1.57
1	1400	7.9 x10^{-13}	2.5 x10^{-5}	9.40	40.67	15.91	26.47	7.56	29.84	9.50	2.10
Varying Fe content, fixed pO_2, pS_2 and temperature,											
5	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.41	39.76	2.59	26.74	8.29	30.22	8.73	1.96
6	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.74	39.85	2.3	25.84	8.58	31.93	9.66	2.17
10	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.62	38.64	2.33	26.56	9.79	30.04	8.69	1.90
11	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.60	37.22	2.12	26.93	10.2	31.96	10.41	2.06
12	1400	1.0 x10^{-15}	2.5 x10^{-5}	7.39	44.64	1.62	27.96	8.50	34.58	6.66	1.48
13	1400	1.0 x10^{-15}	2.5 x10^{-5}	6.10	48.36	2.05	27.54	8.49	37.07	5.35	1.09
14	1400	1.0 x10^{-15}	2.5 x10^{-5}	4.81	52.49	1.59	27.96	8.72	43.11	4.21	0.72
Varying temperature, fixed pO_2 and pS_2											
15	1340	1.0 x10^{-15}	2.5 x10^{-5}	9.55	38.94	15.08	27.16	8.29	30.43	7.43	1.86
5	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.41	39.76	15.63	26.74	8.58	30.22	8.73	1.96
6	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.74	39.85	15.72	25.84	9.79	31.93	9.66	2.17
10	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.62	38.64	15.16	26.56	10.2	30.04	8.69	1.90
11	1400	1.0 x10^{-15}	2.5 x10^{-5}	9.60	37.22	15.88	26.93	11.8	31.96	10.41	2.06
16	1450	1.0 x10^{-15}	2.5 x10^{-5}	9.10	38.52	15.11	25.45	7.25	29.04	8.07	2.00
17	1500	1.0 x10^{-15}	2.5 x10^{-5}	9.73	40.69	16.69	25.63	9.04	28.97	12.19	2.98

Results

The experimental conditions and the analysis of the matte and alloy phases are given in Table I. The oxygen contents of the matte were between 1 and 4.4 wt%, and the Pt contents were between 1.6 and 4.8 wt% and are grouped together with the impurity elements (Co, Cr and Mn), which were not the focus of the current study.

Sulphur activity and sulphur content in the matte

Most of the measurements in the literature on complex Cu-Fe-Ni-S mattes have been performed under conditions where the matte is equilibrated with a H_2/H_2S gas phase and the proportions of Cu to Fe to Ni are fixed and do not vary during equilibration[2-3]. In the present study, the sulphur activity and oxygen activity were fixed and the distribution of the elements between the matte and alloy was established during the reaction/equilibration period. Consequently, for some experiments performed at the same pS_2, there was some variation of the sulphur content of the matte due to small differences in the Fe/Ni ratio and Fe/Cu and Cu/Ni ratios. At the pS_2 of 2.5x10^{-5} atm, the variation of the Fe/Ni wt ratio observed was between 2.65 and 2.54, and the Fe/Cu ratio was between 4.4 and 4.0. Expressed as R_{Fe} and R_{Ni}, ($R_{Fe} = x_{Fe}/(x_{Cu}+x_{Fe}+x_{Ni})$, $R_{Ni} = x_{Ni}/(x_{Ni}+x_{Cu})$ where x is the mole fraction of the species in the matte), these ratios were between R_{Fe} =0.64–0.63 and R_{Ni}=0.64–0.63 respectively. These differences in R_{Fe} and R_{Ni} between experiments occurred from a reaction between the matte and magnesia crucible forming a magnesio-wustite solid solution.

In Figure 2, the activity of sulphur with respect to the gaseous standard state calculated from the equilibrium composition of the gas phase is plotted against the mole fraction of sulphur in the matte and compared with studies on Cu-Fe-Ni-S[1,3] where R_{Fe}, and R_{Ni} are close to the values of this study and the agreement is acceptable. The scatter in this study of the sulphur mole fraction at fixed pS_2 is probably due to the accuracy of determining oxygen in the matte on the SEM, which is a light element and has greater uncertainties than the heavier elements.

Effect of oxygen and sulphur partial pressures, temperature and iron content on the distribution between matte and alloy

In the experimental study, the effect of oxygen partial pressure at fixed sulphur partial pressure and the effect of sulphur partial pressure at fixed oxygen partial pressure were studied. The equilibrium matte chemistry in these experiments did not vary significantly and any changes in the distribution between the matte and alloy ($L^{matte/alloy}$) reflect changes in the alloy chemistry. Also studied were the effect of Fe content in the matte at fixed oxygen and sulphur partial pressures, and temperature.

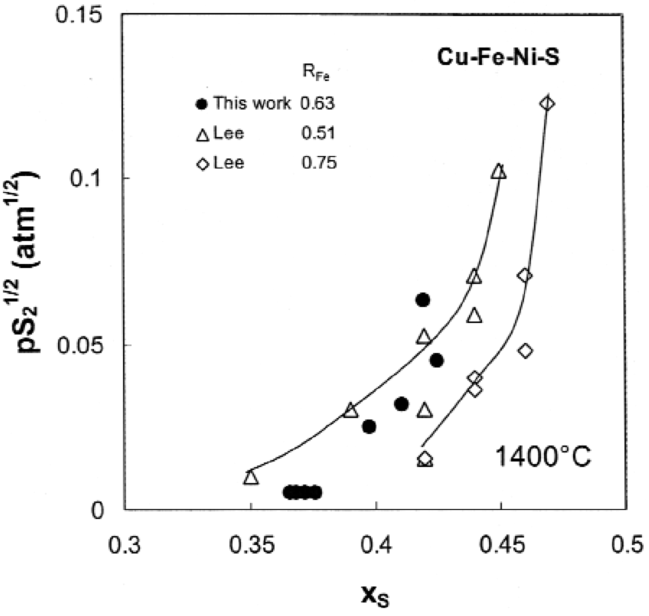

Figure 2. Comparison of the sulphur content in the matte versus the activity of sulphur for Cu-Fe-Ni-S mattes of this study with equilibrium sulphur contents from gas-matte equilibration studies for Cu-Fe-Ni-S mattes with R_{Fe} (0.51 and 0.75) and R_{Ni} (0.5 and 0.75)[3]

The distribution ratio for 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 3. 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 4), the $L_{matte/alloy}$ for Cu, Fe and Ni increased as the pS_2 increased. The Pt distribution between matte and alloy has been shown previously to be independent of the oxygen or sulphur partial pressure[21].

The effect that changing matte chemistry may have on the distribution of Cu, Fe and Ni is shown in Figure 5, where the distribution ratio is plotted against the Fe content in the matte. The Fe and Ni distributions do not change significantly as the matte chemistry changes, but the Cu distribution increased as the Fe concentration increased. Again, the Pt distribution was independent of the iron content in the matte[21].

The effect of temperature at a pS_2 of $2.5x10^{-5}$ atm and pO_2 of 10^{-15} atm on the distribution ratio of Cu, Fe and Ni is shown in Figure 6. The distribution ratio of Cu and Ni decrease as temperature increases and the distribution ratios of Fe increases as temperature increases.

Table II
Matrix of the binary interaction energies (kJ mol^{-1}) deduced for the regular solution model

	Cu	Fe	Ni	Pt
Cu	0	35.8	11.5	-26.6
Fe	35.8	0	-10.3	-100.0
Ni	11.5	-10.3	0	-30.0
Pt	-26.6	-100.0	-30.0	0

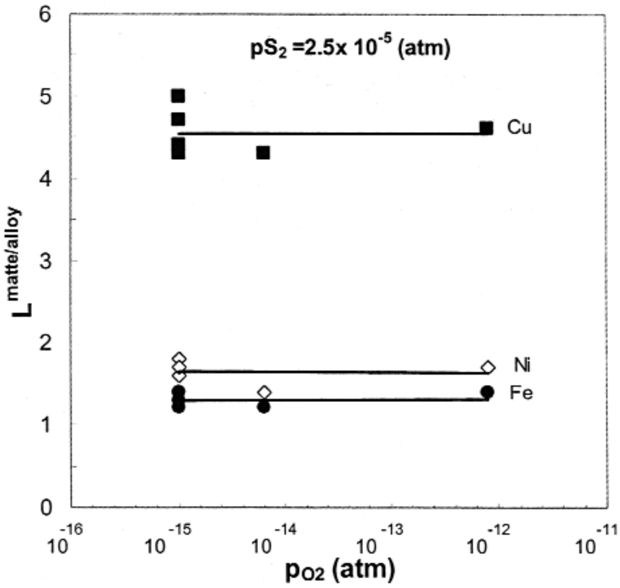

Figure 3 Distribution of Cu, Fe and Ni between the matte and alloy equilibrated at 1400°C and at a fixed sulphur partial pressure as a function of oxygen partial pressure

Discussion

The interaction parameters for a regular solution model have been deduced using the published data on the activity-composition relationship in Pt alloys[21]. The model parameters are given in Table II. The activity coefficients (γ) in the matte were calculated from the activities of Cu, Fe and Ni in the alloy. The standard states for Cu are pure liquid, while for Fe and Ni are pure solid.

The activity of solid iron has also been determined in a study of Fe-Ni-S mattes in equilibrium with Fe-Ni alloy[19] where the activity was calculated by Gibbs-Duhem intergration. The activity of Fe was found to vary with the R_{Fe} ratio and the sulphur content in the matte. The activity of Fe from the Fe-Ni-S study[19] and this work as a function of the sulphur content (for all pO_2 and pS_2 conditions studied) in the matte is plotted in Figure 7. In this study, R_{Fe} was between 0.72 and 0.61, and the calculated activities lie between the bounds of the Fe-Ni-S study where R_{Fe} was 0.5 and 0.75.

Figure 8 shows that at fixed sulphur partial pressure, 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 9 shows that the activity coefficients of Cu, Fe and Ni decrease with increasing sulphur partial pressure. The activity of Cu and Ni in these mattes shows positive departure from ideal behaviour, while that of Fe shows negative deviation.

Somsiri and Gaskell[4] studied the equilibrium between Cu-Fe-S-O mattes and Pt alloys at 1300°C at oxygen partial pressures between $3x10^{-10}$ and $3x10^{-9}$ atm and sulphur partial pressures between $5x10^{-3}$ and $2.5x10^{-2}$ atm. Although not directly comparable (as their system did not contain Ni and the temperature is 100°C lower and the pO_2 and pS_2 ranges are much higher) they found that at constant Fe content in the matte, the activity coefficient of Cu in the matte decreased as the pO_2 increased at fixed sulphur partial pressure. Somsiri and Gaskell also observed that at fixed pO_2, the activity coefficient of Cu in the matte decreased as the pS_2 increased. The activity coefficient of

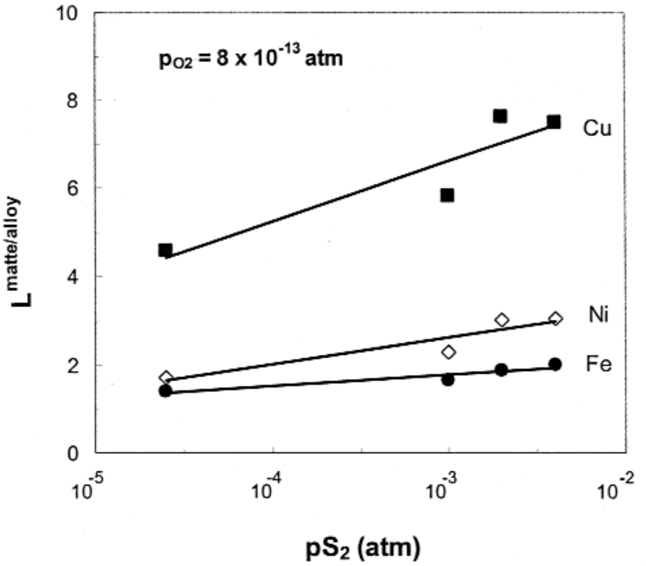

Figure 4. Distribution of Cu, Fe and Ni between the matte and alloy equilibrated at 1400°C and at a fixed oxygen partial pressure as a function of sulphur partial pressure

Fe decreased as the pO_2 increased at fixed sulphur partial pressure, and decreased as the pS_2 increased at fixed pO_2, consistent with the trends of this study.

Somsiri and Gaskell reported that the Cu activity in the matte has a negative deviation from ideal behaviour, which upon first inspection would appear to be inconsistent with this study, where copper has an activity coefficient greater than unity. Other studies on copper mattes[22-24] used the Gibbs Duhem integration method to calculate the activity of Cu and Fe in the matte. The calculated iso-activity diagrams show that for mattes at constant x_{Fe} or x_{Cu}, the activity of Cu (a_{Cu}) and iron (a_{Fe})decreased (and hence γ_{Cu} and γ_{Fe} decreased) as x_S increased, which is consistent with

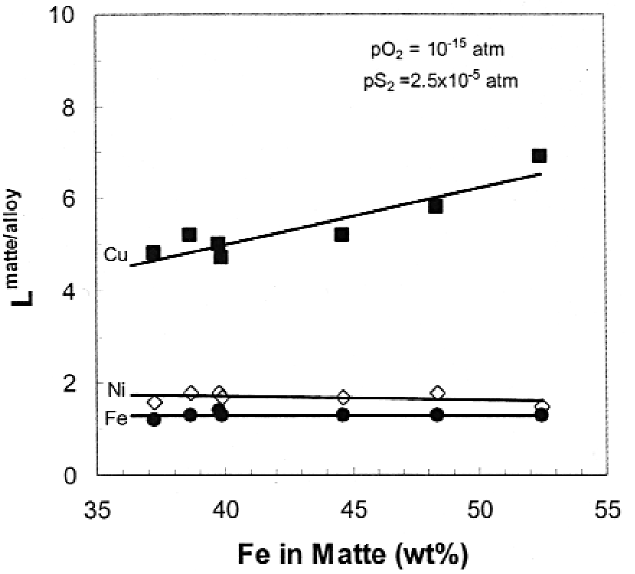

Figure 5. Effect of Fe content in the matte on the Cu, Fe and Ni distribution at pO_2 of 10^{-15} atm and pS_2 of 2.5x10^{-5} atm at 1400°C

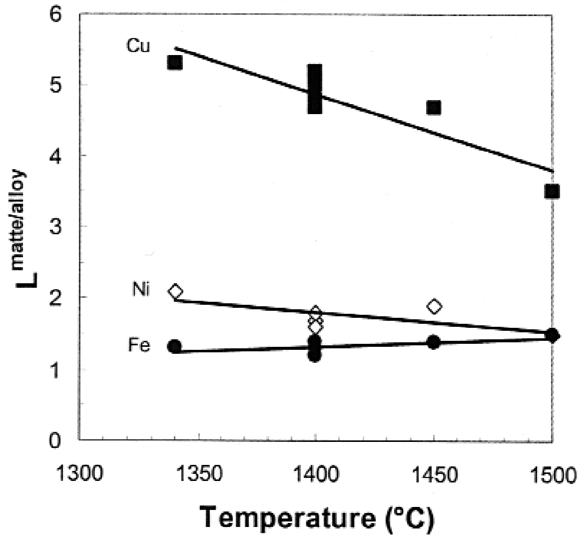

Figure 6. Effect of temperature at a pS_2 of 2.5x10^{-5} atm and pO_2 of 10^{-15} atm on the distribution ratio of Cu, Fe and Ni

the present study. Bale and Toguri[24] determined that γ_{Cu} (where pure liquid Cu was the standard state) had a value of 2.1 at 1200°C, for mattes in equilibrium with solid Fe and have x_s equal to ~ 0.4 (R_{Fe} was between 0.55 and 0.85). The magnitude of the Cu activity coefficient is consistent with the present study. For a matte with x_s of 0.45 and R_{Fe} with a range of 0.82 to 0.63, the calculated a_{Cu} was equal to 0.1, and γ_{Cu} has a range of 1 to 0.5 and decreased as x_{Cu} increased from 0.1 to 0.2[23,24]. The activity of Cu exhibits negative deviation from ideality and the studies on copper mattes at high and low copper activity are consistent

The effect of Fe content in the matte on the activity coefficients of Cu, Fe and Ni from this study are shown in

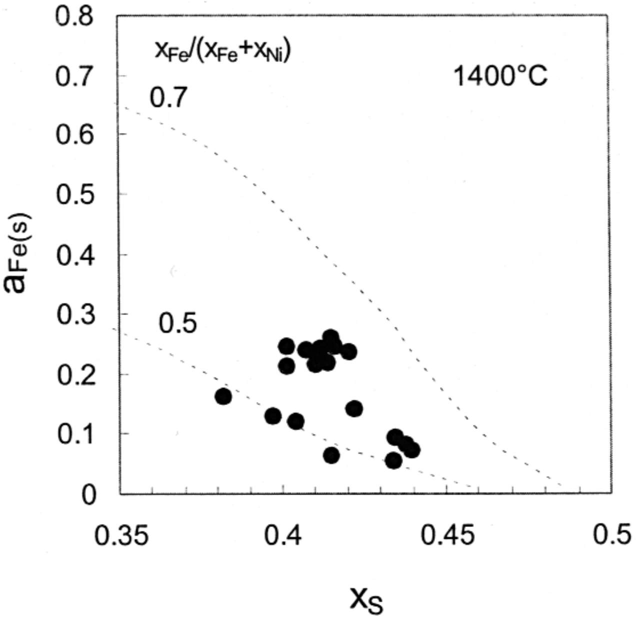

Figure 7. Comparison of the calculated activity of Fe in Fe-Ni-S mattes with this study. Dashed lines are from Conard *et al.*[19] at $x_{Fe}/(x_{Fe}+x_{Ni})$ ratios of 0.5 and 0.75 where the activity of Fe was calculated from Gibbs-Duhem integration (standard state pure solid Fe)

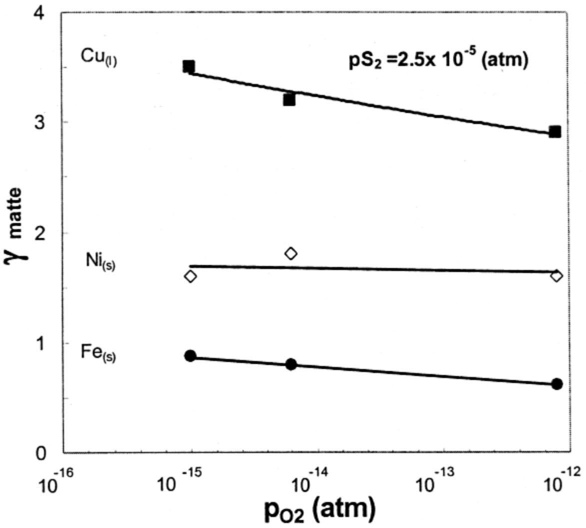

Figure 8. Effect of oxygen partial pressure on the activity coefficient of Cu,Fe and Ni (R_{Fe} = 0.59) in matte at fixed sulphur partial pressure of 2.5x10^{-5} atm and 1400°C. Standard states are with respect to pure liquid for Cu and pure solid for Fe and Ni

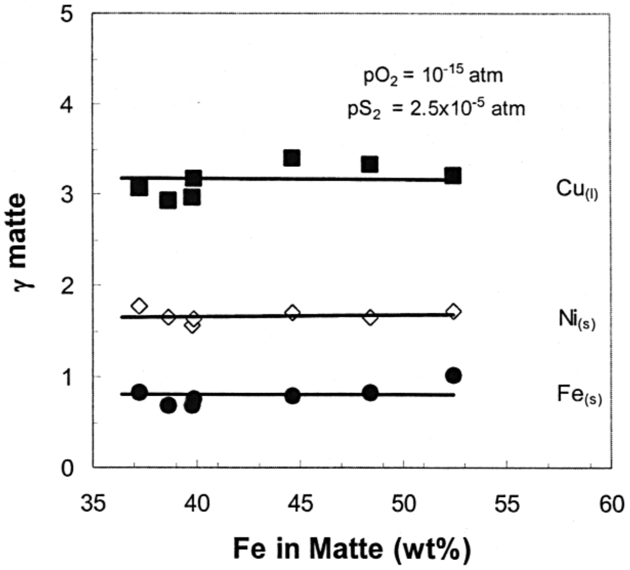

Figure 10. Effect of iron content in the matte on the coefficient of Cu, Fe and Ni in Cu-Fe-Ni-S mattes at 1400°C at pO_2= 10^{-15} and pS_2= 2.5x10^{-5} atm. Standard states are with respect to pure liquid for Cu and pure solid for Fe and Ni.

Figure 10. At fixed oxygen and sulphur pressures the activity coefficients do not vary with Fe content in the matte over the composition range examined. On examination of the iso-activity lines for Fe in Cu-Fe-S mattes[22-24], as discussed above, the activity of Fe decreases as x_s increases. However, for copper mattes that are iron rich and close to iron saturation, the iso-activity lines tend to lie parallel to the lines of constant sulphur mole fraction. For mattes of constant sulphur content, γ_{Fe} then decreases as R_{Fe} increases. At higher x_s, the Fe iso-activity lines lie parallel to the Cu_2S-FeS join. Then if x_s is constant, a_{Fe} and γ_{Fe} increase as R_{Fe} increases. At intermediate sulphur contents and iron activities, there is a range of iron contents where γ_{Fe} is constant and does not vary with R_{Fe}, consistent with the results of this study. In this composition region, the copper isoactivity lines also lie parallel to the lines of constant x_{Cu} and γ_{Cu} is constant with a value of close to 2.

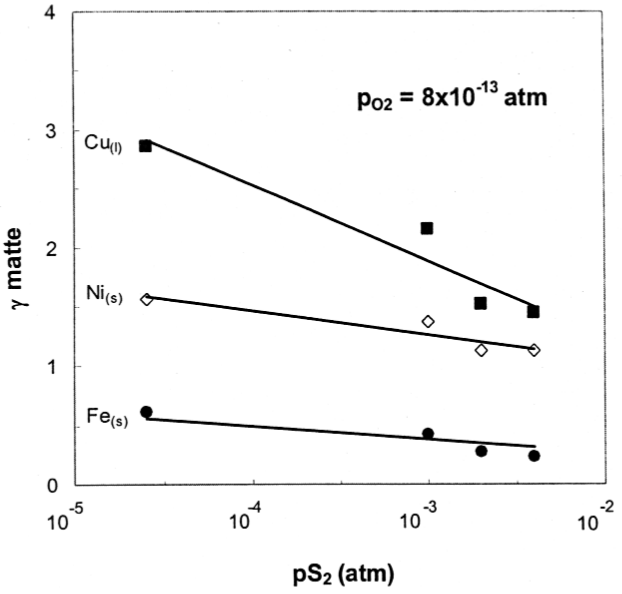

Figure 9. Effect of sulphur partial pressure on the activity coefficient of Cu, Fe and Ni (R_{Fe} = 0.59) in matte at fixed oxygen partial pressure of 8x10^{-13} atm and 1400°C. Standard states are with respect to pure liquid for Cu and pure solid for Fe and Ni

The effect of temperature at a pS_2 of 2.5x10^{-5} atm and pO_2 of 10^{-15} atm is shown in Figure 11 and over the temperature range studied, γ_{Cu}, γ_{Fe}, and γ_{Ni} were constant. This is consistent with the literature for the γ of Fe and Ni in the Fe-Ni-S system[25] and Fe and Cu in the Cu-Fe-S system are nearly independent of temperature over the temperature range of 1200–1400°C[23].

Conclusions

The equilibrium distribution of Cu, Fe and Ni in Cu-Fe-Ni mattes and solid Pt alloys was studied over a temperature range of 1340 to 1500°C. For a matte containing 45% Fe, 11% Ni, 8% Cu, at 1400°C, the following behaviour was observed for the distribution ratios of Cu, Fe and Ni:

- Under the range of sulphur and oxygen pressures of this study where pS2 =2.5x10^{-5} atm and pO_2 was between 10^{-15} and 10^{-12} atm, the distribution ratios of Cu, Fe and Ni between matte and alloy were independent of oxygen pressure and had values of 4.5, 1.6 and 1.2 respectively.
- The distribution ratio of 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 7.8, 2.1 and 3 respectively when pS_2 = 8x10^{-3} atm.
- The Cu and Ni distribution ratios decreased with increasing temperature and the Fe distribution ratio increased slightly with temperature over the temperature range of 1350–1500°C.

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 Fe and Ni distribution appeared to be independent of the iron content in the matte and had a value of 1.2 and 1.6 respectively.

Comparison of the mole fraction of sulphur in the matte with the activity of S_2 in the gas phase was in accord with

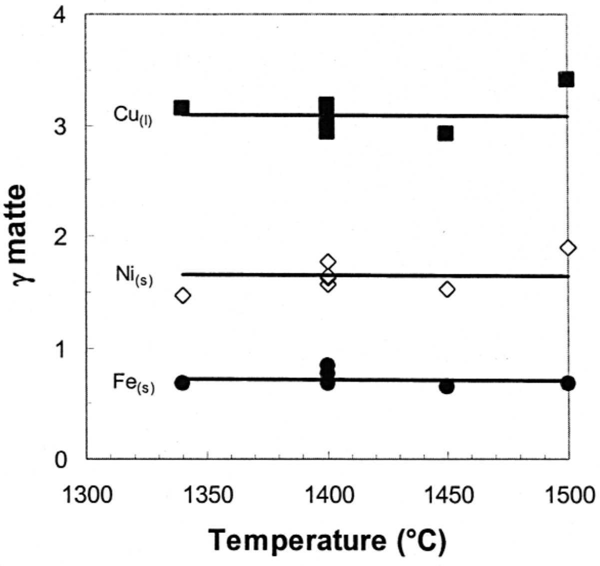

Figure 11. Effect of temperature at a pS_2 of $2.5x10^{-5}$ atm and pO_2 of 10^{-15} atm on activity coefficient of Cu, Fe and Ni in matte. Standard states are with respect to pure liquid for Cu and pure solid for Fe and Ni

other studies on Cu-Fe-Ni-S and Fe-Ni-S with similar Fe:Ni ratios and Cu:Ni ratios. The activity of Cu, Fe and Ni in the matte was calculated from a regular solution model for a Cu-Fe-Ni-Pt alloy. The activity of Cu and Ni in the matte showed positive deviation from ideal behaviour, while that of Fe showed negative deviation. It was found that the activity coefficients in the matte behaved in the following manner:

- At fixed sulphur partial pressure, γ_{Ni} was found to be independent of the oxygen partial pressure and had a value of 1.6. The activity coefficients of γ_{Fe} and γ_{Cu} decreased as pO_2 increased, from 0.85 to 0.64 and 3.5 to 2.9 respectively;
- At fixed oxygen partial pressure, γ_{Cu}, γ_{Fe} and γ_{Ni} decreased as the sulphur partial pressure increased;
- Over the temperature range of 1350–1500°C at a pS_2 of $2.5x10^{-5}$ atm and pO_2 of 10^{-15} atm, γ_{Cu}, γ_{Fe} and γ_{Ni} remained constant;
- For mattes where the ratio of Cu to Ni was kept constant at 0.6, γ_{Cu}, γ_{Fe} and γ_{Ni} were also independent of the iron content of the matte at a pS_2 of $2.5x10^{-5}$ atm and pO_2 of 10^{-15} atm.

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