The distribution of metallic elements in granulated nickel converter matte phases

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Keywords: Pyrometallurgy, converter, nickel, matte, distribution

Abstract – Metallic elements occupy a wide range in granulated nickel converter matte phases. The distribution of these metallic elements, particularly during crystallization path events, appears to be poorly understood. The present study serves to investigate the distribution of Fe, Co, Ni, Cu, and Pb between nickel-sulphide, copper-sulphide, and alloy phases. A novel combination of thermo-chemical modelling, electron microscopy, and electron probe microanalysis was applied to understand crystallization path events and the associated metallic element distribution. This study has demonstrated that major Ni incorporated during copper-sulphide crystallization would serve to mobilize minor Co towards distribution in copper-sulphide phases. In addition, solid solution substitution of Cu by Ni is manifested by compositional zoning of copper-sulphide phases. The role played by Ni during alloy crystallization suggests that minor Co was also mobilized, along with an increase in principal Ni. Fe, by contrast, seems to be incompatible with principal Ni. In addition, solid solution substitution of Ni with PGEs and Cu is manifested by compositional zoning of NiCu-alloy phases.

INTRODUCTION

Industrial mattes associated with the pyrometallurgical Peirce-Smith nickel converting process (in the South African context) can invariably be characterised by the multi-component, complex nature of the Ni-Cu-Fe-S system, along with low concentrations of many other elements including Co, Pb, and PGEs (platinum group elements). The deliberate control of a specific iron-endpoint (intrinsically linked to sulphur-endpoint) during the converting process must be a required precursor to producing melts of uniform chemical composition and associated properties. At Lonmin, Western Platinum, the converter matte is granulated in water, and the process can be regarded as fast cooling.

There is particular significance in the analysis of metallic elements in granulated nickel converter matte phases from an industrial matte sample with

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a reported low iron-endpoint of 0.15% by mass. Closely related previous studies have underscored the fact that metallic elements occupy a wide range in, particularly, hexagonal (rhombohedral) heazlewoodite, tetragonal chalcocite, and face-centred cubic alloy type structures. For this reason, an investigation is required into the distribution of the transition elements (Fe, Co, Ni, and Cu) and the heavy element, Pb, between nickel-sulphide, copper-sulphide, and alloy phases. It is further relevant to contrast actual and equilibrium trace, minor, and major metallic element distributions as an indication towards the true conditions of crystallization. In addition, the resultant microstructures form a primary part of the processing characteristics of the host phases.

CHEMICAL COMPOSITION OF SULPHIDE PHASES

Electron probe microanalysis was essential to a comprehensive compositional investigation. For this purpose, electron probe microanalysis was performed on representative analytical sub-samples with a Cameca SX50 microprobe, equipped with four wavelength dispersive spectrometers and an energy dispersive spectrometer. The system was calibrated using reference standards of pure Fe, Co, Ni, Cu, Pb, Pd, Pt, Rh, Ru, Ir, and Os, and a pyrrhotite (FeS) reference was used for S. The analysis was performed exclusively on wavelength dispersive spectrometers. The analytical precision was limited by the approximately 2 μm beam diameter, associated interaction volume, size and heterogeneity of the analysed structures. A complete description of the analytical technique can be found in Thyse[1] et al., (2010). All percentages are in mass% unless otherwise indicated.

Distribution of metallic elements in nickel-sulphide phases

Twenty-two point analyses with respect to massive indistinguishable heazlewoodite type structures on a selection of particles confirms the presence of invariably Ni-rich, relatively S-poor phases. The principal compositional range of Ni (with respect to the twenty-two point analyses) averages 66.56%, but varies between 60.52% and 71.08%. The S concentration varies between 17.66% and 26.80%, with an average of 23.34%. Table I reports the average concentrations for the major, minor and trace metallic elements distributed in the probed nickel-sulphide phases.

Table I: Average metallic element distribution in ppm with respect to nickel-sulphide phases

Element	Detection Limit (ppm)	Phases below [*]D.L.	Phases Analysed	Average Analysis (ppm)
Cu	700	1	21	54 908
Co	200	None	22	4 757
Pb	1200	1	21	2 119
Fe	200	None	22	877

[*]**D.L.** - Detection Limit

Most of the phases probed contain major Cu with concentrations varying between a minimum of 0.97% and a maximum of 13.84%. Co, Pb, and Fe concentrations vary between minima of (1 982, 1 309, and 296 ppm) and maxima of (6 796, 2 950, and 2 638 ppm), respectively. It is important to note that the concentrations for this study refer to the analysis at the core of the respective phases. Additionally, minor and trace PGEs distributed in nickel-sulphide phases are reported in Thyse[1] et al., (2010).

Distribution of metallic elements in copper-sulphide phases
The nickel-sulphide phases form a cementing matrix embedding well-rounded chalcocite type structures, as shown in Thyse[2] et al., (2010). Eighteen point analyses with respect to the chalcocite type structures on various particles confirm the presence of invariably Cu-rich, relatively S-poor phases. The principal compositional range of Cu (with respect to the eighteen point analyses) averages 71.32%, but varies between 65.92% and 76.57%. The S concentration averages 20.12%, but varies between 19.22% and 20.76%.

Table II reports the average concentrations for the major and minor metallic elements distributed in the probed copper-sulphide phases.
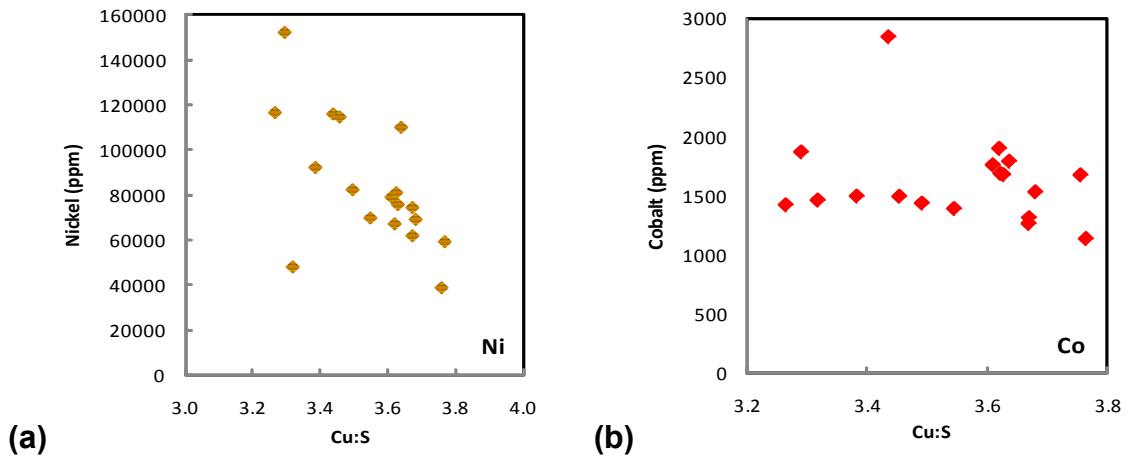
Table II: Average metallic element distribution in ppm with respect to copper-sulphide phases

Element	Detection Limit (ppm)	Phases below [*]D.L.	Phases Analysed	Average Analysis (ppm)
Ni	700	None	18	84 155
Co	200	None	18	1 625
Fe	200	None	18	1 253

[*]**D.L.** - Detection Limit

All the phases probed contain major Ni, with concentrations varying between a minimum of 3.92% and a maximum of 15.23%. Co and Fe concentrations vary between minima of (1 144 and 521 ppm) and maxima of (2 844 and 7 302 ppm), respectively. In contrast (to nickel-sulphide phases), the copper-sulphide phases appear to be Pb-poor, as no detectable concentrations were present.

Figure 1 considers (with respect to copper-sulphide phases) the Ni and Co specific concentrations in relation to the Cu:S inter-element ratio.

Figure 1: Metallic element-specific concentrations in ppm, in relation to the Cu:S ratio for (a) Ni and (b) Co

The trend for Figure 1a suggests a strong decrease in Ni concentration with a moderate increase in Cu:S ratio. In comparison, the trend for Figure 1b suggests a weak decrease in Co concentration with a moderate increase in Cu:S ratio.

CHEMICAL COMPOSITION OF ALLOY PHASES

Eighteen point analyses with respect to alloy type structures on a selection of particles confirms the presence of invariably NiCu-dominant, relatively S-deficient phases. The principal compositional ranges of Ni and Cu (with respect to the eighteen point analyses) average 52.70% and 25.15%, but vary between (42.91% and 63.47%) and (14.66% and 36.79%), respectively. The S concentration varies between 1.76% and 14.97%, with an average of 7.34%.

Table III reports the average concentrations for the minor metallic elements distributed in the probed NiCu-alloy phases.

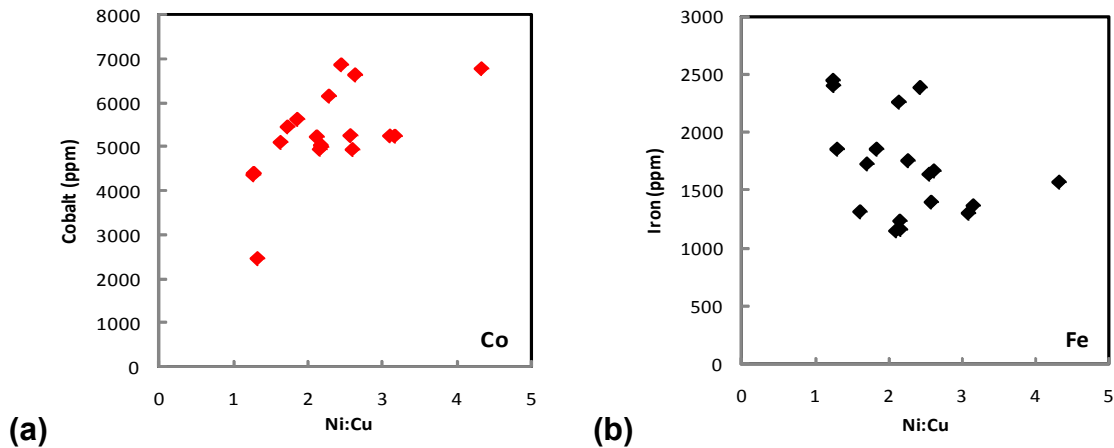**Table III:** Average metallic element distribution in ppm, with respect to NiCu-alloy phases

Element	Detection Limit (ppm)	Phases below *D.L.	Phases Analysed	Average Analysis (ppm)
Co	200	None	18	5 270
Pb	1200	1	17	2 420
Fe	200	None	18	1 693

*D.L. - Detection Limit

All the phases probed contain minor Co and Fe, with concentrations varying between minima of (2 465 and 1 151 ppm) and maxima of (6 874 and

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2 444 ppm), respectively. The Pb concentration varied between a minimum of 1 564 ppm and a maximum of 9 464 ppm. The major and minor PGEs distributed in the NiCu-alloy phases are also reported in Thyse[1] et al., (2010).

Figure 2 considers (with respect to NiCu-alloy phases) the Co and Fe specific concentrations in relation to the Ni:Cu inter-element ratio.
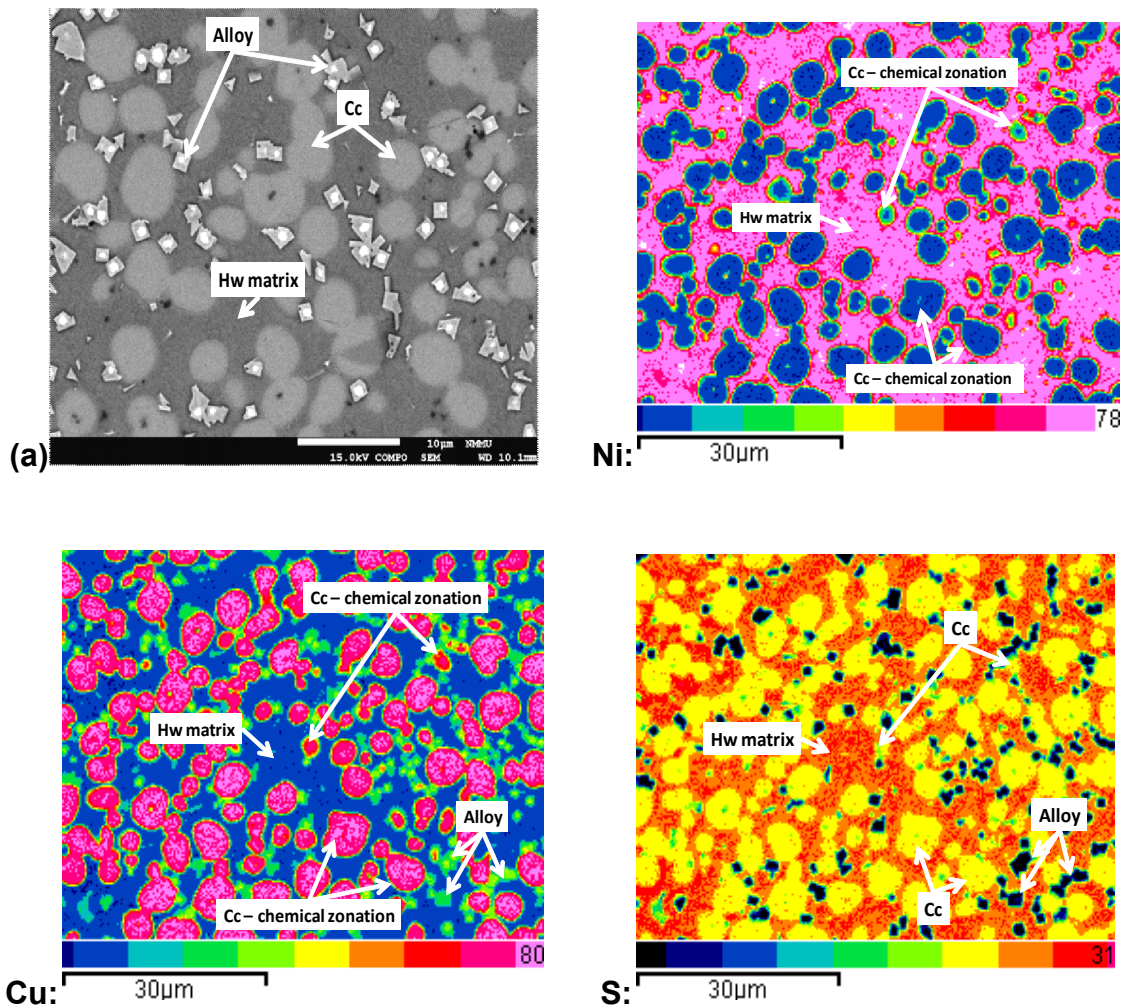

Figure 2: Metallic element-specific concentrations in ppm, in relation to the Ni:Cu ratio for (a) Co and (b) Fe

The trend for Figure 2a suggests an increase in Co concentration with an increase in Ni:Cu ratio. In contrast, the trend for Figure 2b suggests a decrease in Fe concentration with an increase in Ni:Cu ratio.

COMPOSITIONAL VARIATION

The variation in major and principal elements within and between respective phases were characterised using a JEOL JSM-7001F FEG SEM employing compositional imaging, and EDS-induced high-resolution element-specific phase mapping. An accelerating voltage of 15 kV and probe current of 90 µA proved optimal for this purpose. Figure 3 provides penetrative illustrations of phase morphology and the major and principal Ni, Cu, and S distributions.

The compositional micrograph, shown in Figure 3a, provides indication of a complex intergrowth relationship between the nickel-sulphide (Hw) matrix, copper-sulphide (Cc), and NiCu-alloy phases. Figure 3b maps (in false colour contrast) the Ni distribution within and between the relevant phases. The marked specificity of principal Ni distributed within the nickel-sulphide matrix is particularly noteworthy. Moreover, the contact between the nickel-sulphide matrix and copper-sulphide phases can distinctly be characterised by a thin border zone of smaller principal Ni content. The copper-sulphide phases also exhibit compositional zonation with the major Ni distribution increasing away from the core.

Figure 3: SEM-induced (a) compositional micrograph at 10 µm scale bar (b) phase-related Ni distribution map (c) phase-related Cu distribution map (d) phase-related S distribution map at 30 µm scale bar, respectively
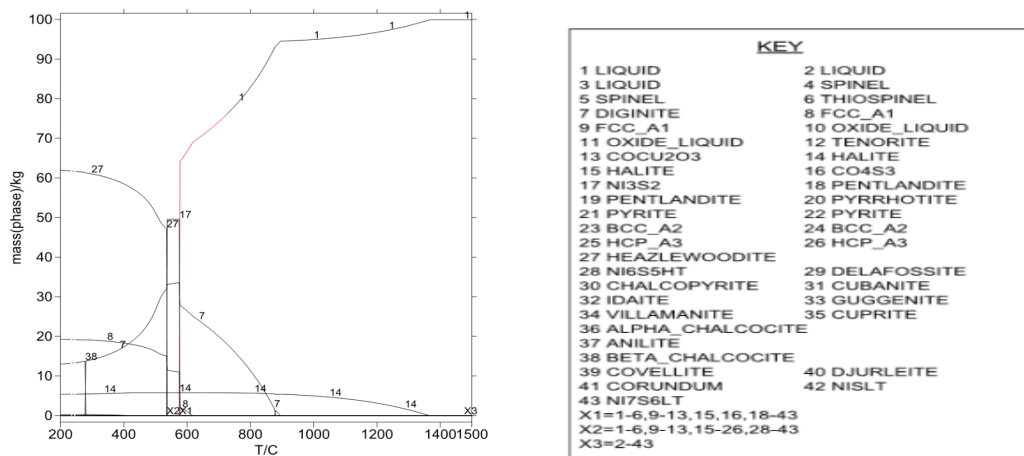
Figure 3c maps the Cu distribution within and between the related phases. The copper-sulphide phases exhibit compositional zonation, with the principal Cu distribution generally decreasing away from the core. The mapping also reveals that the core of NiCu-alloy phases can contain more Cu in relation to the rim, as well as in comparison with the adjacent nickel-sulphide matrix.

Figure 4c maps the S distribution within and between the related phases. The mapping reveals that considerably more variable S can be associated with nickel-sulphide phases. In addition, the core of the NiCu-alloy phases contains considerable less S than the rim of the phases.

EQUILIBRIUM CRYSTALLIZATION PATHS

The crystallization of sulphide and alloy phases from a parent sulphide matte is an important event influencing the phase-specific major, minor, and trace metallic distributions.

Equilibrium crystallization paths were generated with MTDATA, supported by the Mtox matte database[3], for the low iron-endpoint of interest. The database contains assessed thermodynamic descriptions for the matte system Co-Cu-Fe-Ni-O-S, and thus allows calculations of the equilibrium properties of the phase assemblages from metal-saturated mattes and solid sulphide, to oxide-saturated systems. The equilibrium crystallization paths present masses of stable phases as a function of temperature, over a temperature interval of 200–1500°C, as shown in Figure 4a.

Figure 4: MTDATA solidification simulation showing (a) masses of stable phases as a function of temperature (b) enclosed key in support of phase numbers

Figure 4a indicates the early crystallization of a halite-type (Na-Cl structure) solid solution (phase 14) consisting mainly of NiO, forming at approximately 1380°C and constituting 6% of the total mass.

The primary crystallization of digenite (phase 7), particularly relevant to this study, occurs at 878°C, with continued solidification upon cooling to 280°C. Extracted MTDATA phase-specific compositional data reveals the principal compositional range of Cu varies between 77.14–79.19% for the temperature interval 878°C–280°C. The S concentration varies between 20.68–20.27% for the respective temperature interval. Furthermore, metallic elements commonly incorporated in the digenite equilibrium assemblages decrease from 1.72–0.42% Ni, 4039–1128 ppm Co, and 578–5 ppm Fe during the respective temperature interval. These distributions were obtained from extracted MTDATA phase-specific compositions. The high-temperature digenite phase inverts to beta-chalcocite (phase 38) at 278°C, with minimal compositional modification upon cooling to 200°C. Extracted compositional data reveals the beta-chalcocite phase to consist of 79.85% Cu and 20.15% S. The beta-chalcocite phase constitutes approximately 13% of the total mass.

An alloy phase (8) crystallizes at approximately 616°C and is characterized by significant development in mass at distinct temperatures and finally constitutes 18% of the total mass.

The primary crystallization of Ni_2S_3 (phase 17), largely relevant to this study, occurs at 575°C, with continued solidification upon cooling to 538°C. Extracted MTDATA phase-specific compositional data reveals the principal compositional range of Ni varies modestly between 74.51–74.38% for the temperature interval 575°C–538°C. The S concentration varies modestly between 24.70–24.92% for the respective temperature interval. In addition, metallic elements regularly incorporated in the Ni_2S_3 equilibrium assemblages decrease from 5469–4383 ppm Cu, and minimally 7–4 ppm Fe. In contrast, Co increases modestly from 2437–2472 ppm.

The eutectic temperature is predicted to occur just below 575°C, with subsequent parent sulphide matte consumption. The high-temperature Ni_2S_3 phase inverts to heazlewoodite (phase27) at 535°C, with minimal compositional modification upon cooling to 200°C. Extracted compositional data indicates the heazlewoodite consists of 73.20–73.25% Ni and 26.70% S. The heazlewoodite phase constitutes approximately 63% of the total mass.

DISCUSSION

The results obtained from this study serve to develop an understanding of the distribution of metallic elements during crystallization path events.

Nickel-sulphide phases
Melt composition is probably the most important process variable influencing the phases formed[4], their composition, and relative abundance. Bulk chemical analyses indicate a slightly lower Ni:S ratio of 2.5 as compared to the average phase-specific compositional ratio of 2.9 as determined from electron probe microanalysis.

The principal constituents of the analysed nickel-sulphide phases (Ni and S) fluctuate considerably. These fluctuations reflect the variable presence of metallic elements incorporated in the nickel-sulphide structures, in particularly Cu. As a consequence, the nickel-sulphide phases exhibit considerable non-stoichiometry. The theoretical nickel-sulphide or heazlewoodite phase data, as indicated by the MTDATA equilibrium assemblages at 200°C, suggest a composition close to 73.25% Ni, 26.70% S, and 1 021 ppm Co. It therefore seems reasonable to suggest that non-equilibrium copper-enriched nickel-sulphide phases are a common characteristic of this particular low iron-endpoint matte system. Electron probe microanalysis indicates the maximum solubility of Cu in nickel-sulphide phases as 13.84%.

The variable composition of both principal Ni and major Cu, suggests that mutual solid solubility warrants consideration. In addition, complete solubility between Ni and Cu is obvious from Cu-Ni phase diagrams, as both have the same crystal structure (face-centred cubic), nearly the same radii, electronegativity, and valence. It therefore seems reasonable to suggest that major Cu represents atomic substitution of Ni by Cu.

Minor Co, Pb, and trace Fe appear to co-exist with principal Ni and S, major Cu and PGEs, within the nickel-sulphide phases. The distribution of the metallic elements was most likely established during the crystallization path events with respect to nickel-sulphide phases. The primary crystallization of Ni_2S_3 occurs at 575°C, with continued solidification upon cooling to 538°C. The Ni_2S_3 phase inverts to heazlewoodite at 535°C, with minimal compositional modification upon cooling to 200°C. The distribution of available metallic elements between nickel-sulphide and alloy assemblages would have occurred for a very short temperature range until the eutectic event.

Copper-sulphide phases
The comparative Cu:S ratio (1.5) for the bulk matte is significantly lower than indicated for the average phase-specific compositional ratio (3.5) as determined from electron probe microanalysis.

Cu occurs both in the primary nickel-sulphide phase and as the principal constituent of copper-sulphide phases in addition with S. The principal constituents of the probed copper-sulphide phases vary considerably as well. The variations in Cu and S suggest the characteristic presence of major Ni, and minor Co and Fe, within the copper-sulphide structures, and exhibit non-stoichiometry. The theoretical copper-sulphide phase data, as shown by the MTDATA phase assemblages at 200°C, suggest a composition close to 79.85% Cu and 20.15% S. This seems to imply that non-equilibrium nickel-enriched copper-sulphide phases are a characteristic feature of the matte system. There appears to be on average more Ni (8.42%) in copper-sulphides, than Cu (5.49%) in nickel-sulphides. Electron probe microanalysis indicates the maximum solubility of Ni in copper-sulphide phases as 15.23%. The distribution of Ni in copper-sulphide phases appears to be a strong function of the variable Cu:S ratio. Microanalytical data suggest that a decrease in Ni concentration can be associated with an increase in Cu:S ratio (see Figure 1a).

The variable composition of principal Cu and major Ni suggests that mutual solid solubility is relevant. Major Ni would therefore represent atomic substitution of Cu by Ni. In addition, compositional zonation, as shown in Figure 3c, supports the submission that metallic elements are probably incorporated within the copper-sulphide phases in solid solution.

Minor Co and Fe appear to co-exist with principal Cu and S, major Ni, and PGEs, within the copper-sulphide phases. Microanalytical data suggest that a modest decrease in Co can be associated with an increase in Cu:S ratio (see Figure 1b), facilitated by the increase in principal Cu. This seems to suggest that Co and Ni display compatible distribution behaviour in the copper-sulphide phases.

The distribution of the metallic elements was most likely established during the crystallization path events with respect to copper-sulphide phases. The equilibrium crystallization path, as simulated by MTDATA, indicates that the primary crystallization of digenite occurs at 878°C, with continued solidification

upon cooling to 280ºC. Digenite inverts to beta-chalcocite at 278ºC, with minimal compositional modification upon cooling to 200ºC. The distribution of available elements between phase assemblages for copper-sulphide, alloy, and nickel-sulphide would have occurred for a very short temperature range until the subsequent consumption of the parent matte. It seems reasonable to suggest that the presence of major Ni controls the Co budget of copper-sulphide phases.

NiCu-alloy phases
The comparative Ni:Cu ratio (1.7) for the bulk matte is slightly lower than indicated for the average phase-specific compositional ratio (2.1) as determined from electron probe microanalysis.

Ni occurs as the principal constituent of primary alloy phases, nickel-sulphide phases, and as major element in primary copper-sulphide phases. Cu occurs as the principal constituent of primary alloy phases, copper-sulphide phases, and as major element in primary nickel-sulphide phases. The S concentration for alloy phases varies between a minimum of 1.76% and a maximum of 14.97%, and its presence appears to be a strong function of the total metallic elements incorporated in the alloy phases. In addition, characteristic variation of the principal Ni and Cu concentrations suggest the incorporation of minor Co, Pb, Fe, and major PGEs.

The variable composition of principal Ni and Cu, including PGEs, suggests that mutual solid solubility is relevant. Major PGEs in association with Cu would therefore represent atomic substitution of Ni with PGEs and Cu in the alloy structure. Compositional zonation, as shown in Figure 3c, supports the submission that Cu is probably incorporated within the alloy structures in solid solution. Moreover, high-resolution bright-field TEM images[1] show that major PGEs are probably incorporated within the alloy structure in solid solution.

The distribution of Co (see Figure 2a) suggests an increase in element-specific concentration with an increase in Ni:Cu ratio. The trend is in good agreement with the distribution for Co in copper-sulphide phases. In contrast, the distribution for Fe (see Figure 2b) indicates a decrease in element-specific concentration with an increase in Ni:Cu ratio. Furthermore, there seems to be a strong correlation between Fe in the bulk matte (0.15%) and the phase-specific average (0.17%). It seems reasonable to suggest that the increase in Ni:Cu ratio, facilitated by progressive Ni diffusion from parent matte to alloy structures, controls the Co budget of alloy phases. In contrast, a decrease in Ni:Cu ratio, facilitated by progressive Cu diffusion from Cu-enriched matte to alloy structures, would control the Fe budget of the alloy phases.

CONCLUSIONS

The nickel-sulphide, copper-sulphide, and NiCu-alloy phases include evidence of phase-specific metallic element heterogeneities. In addition, the distribution of the metallic element heterogeneities during crystallization path events

appears to be poorly understood. The present study has demonstrated that major Ni incorporated during copper-sulphide crystallization would serve to mobilize minor Co towards distribution in copper-sulphide phases. In addition, solid solution substitution of Cu by Ni is manifested by compositional zoning of copper-sulphide phases. Constraints on the distribution of these elements can be placed by evidently increasing the Cu:S ratio of the respective phases. This can perhaps be done by improving the control of the bulk matte composition.

The role played by Ni during alloy crystallization suggests that minor Co was also mobilized along with an increase in principal Ni. Fe, in contrast, seems to be incompatible with principal Ni. In addition, solid solution substitution of Ni with PGEs and Cu is manifested by compositional zoning of NiCu-alloy phases. It could perhaps be significant to place constraints on the Ni:Cu ratio, thereby allowing the alloy phases to act as primary collectors for the available PGEs. This could improve the metallurgical quality of the matte and impact positively on subsequent processing.

ACKNOWLEDGEMENTS

REFERENCES

1. E.L. Thyse, G. Akdogan, J.H. Neethling, E.J. Olivier, P. Taskinen, and J.J. Eksteen, Partitioning of PGEs in nickel converter matte phases: direct observations by electron microscopy and electron probe microanalysis, Process Mineralogy '10, Vineyard Hotel, Cape Town, Minerals Engineering International, 2010.
2. E.L. Thyse, G. Akdogan, and J.J. Eksteen, in press, The effect of changes in iron-endpoint during Peirce-Smith converting on PGE-containing nickel converter matte mineralization, Minerals Engineering. doi: 10.1016/j.mineng.2010.09.022.
3. J. Gisby, A. Dinsdale, and P. Taskinen, Predictive thermochemistry of oxide and sulfide systems, Proc. EMC 2007 (Vol. 4), Düsseldorf, 11–14 June 2007, GDMB, Clausthal-Zellerfeld, 2007, pp. 1721-1736.
4. P. Hayes, Process Principles in Minerals & Materials Production, 3rd edition, Hayes Publishing, 2003.

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