Towards understanding nickel converter matte solidification

E.L. Thyse [a,*], G. Akdogan [a], P. Taskinen [b], K.S. Viljoen [c], J.J. Eksteen [d]

[a] University of Stellenbosch, Department of Process Engineering, Private Bag XI, Matieland 7602, South Africa
[b] Aalto University, School of Science and Technology, PO Box 16200, FI-00076 Aalto, Finland
[c] University of Johannesburg, Department of Geology, Johannesburg 2000, South Africa
[d] Western Australian School of Mines, GPO Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

ABSTRACT

Nickel converter mattes are complex metallurgical solutions of Ni, Cu, S, Fe and O along with low concentrations of many other elements including Co, Pb and PGEs. Studies on how such complex mixed solutions evolve upon cooling may contribute towards an improved understanding of matte solidification. Liquidus and primary phase equilibria were calculated for Cu–Ni–S ternaries including fixed iron and cobalt concentrations. True liquid matte starting compositions and calculated assays were subsequently superimposed on relevant Cu–Ni–S_FeCo ternary systems. Multiphase cooling equilibria were also calculated for variable Cu–Ni–S–Fe–Co–O matte systems. In addition, actual industrial mattes were analysed using automated mineralogy, electron probe microanalysis and field emission scanning electron microscopy.

The effect of the end composition of the ternary systems at fixed iron and cobalt concentrations on the liquidus temperature range has been quantified. The liquidus temperature range is lowered when the fixed iron and cobalt concentration decreases. The solidification pathway of oxygen-free liquid matte has been estimated. Moreover, it has been shown that variations in the starting composition of oxygen-free matte alter the path of solidification towards the eutectic. The examination of multiphase cooling equilibria for variable Cu–Ni–S–Fe–Co–O liquid phase systems provided a quantitative understanding of solidification processes to within ±2.5 °C. The analysed nickel and copper-sulphide phase structures have shown to exhibit chemical non-equilibrium within high and low iron matte. It can be concluded that the present study has provided a coherent insight into nickel converter matte solidification processes.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The converting of nickel mattes has been achieved for more than hundred years and the general principles of the process appear to be understood (Kyllo and Richards, 1991). Converter matte is usually blown by air or oxygen and resultant iron with intrinsically linked sulphur endpoints are considered as a function of the extent of blow. An important process variable in converting conditions is optimising the composition of the matte with respect to iron and sulphur endpoints. Further endpoint considerations would depend on downstream processing requirements.

Nickel converter mattes (in the South African context) could be slow cooled to enhance magnetic separation of the base metal alloy phases and associated platinum group metal alloys from nickel-sulphide and copper-sulphide phases prior to hydrometallurgical processing. As a result there has been considerable effort to understand, via experimental investigations (Viljoen, 2001), the effect of variable starting compositions on the slow cooled Cu–Ni–S system.

The experimental investigations were limited to a temperature range. A notable finding is the difference in solidification path of liquid matte as a function of variable starting iron content and temperature. Matte slow cooling processes and resultant microstructures were extensively investigated (Schouwstra, 2003) and are commonly applied within the industrial context of the Anglo Platinum beneficiation route.

Nickel converter mattes could also be fast cooled by means of granulation prior to hydrometallurgical processing. Lonmin (Western Platinum) operates three Peirce–Smith converters and fast cooling processes are applied within the framework of their beneficiation route (Eksteen, 2011). There has been limited effort to understand the effect of variable starting compositions on fast cooled nickel matte systems, particularly via direct experimental investigations. A recent study (Thyse et al., 2011a) assessed in several details the effect of differing iron endpoints on PGE-containing base matte mineralisation upon fast cooling from actual production samples. As a result several aspects related to matte mineralisation can at present be explained for such systems.

To this effect some measure of understanding of liquid matte solidification has been achieved, but many details remain

unknown. This study is therefore concerned with consolidating the understanding developed and to examine in greater detail the intricacies of nickel converter matte solidification and processes that occur within via reference to equilibrium systems of variable composition and phase structures associated with fast cooled industrial mattes.

2. Methods

Mattes are complex metallurgical solutions of Ni, Cu, S, Fe and O along with low concentrations of many other elements including Co, Pb and PGEs. It was required to initiate predictive equilibrium calculations specific to endpoint correlated multi-component systems for examination of equilibrium cooling processes for such metallurgical solutions. The main assumption underpinning the predictive calculations is phase and chemical equilibria could be calculated reliably from critically assessed structural, thermodynamic and phase equilibrium measurements using MTDATA phase diagram software from the National Physical Laboratory, UK (NPL) (Davies et al., 2002). The thermodynamic data used in the calculations was extracted from the extensive and critically assessed Mtox database which has been validated earlier in a number of industrial and phase diagram case studies dealing with sulphide smelting (Gisby et al., 2002, 2007; Taskinen et al., 2005). The sulphide phases have been modelled in the database as non-ideal solutions using an associate model for the molten phase (Barry et al., 1993) and a sublattice model (Barry et al., 1992) of type $(Co_{1/2},Cu,Fe_{1/2},Ni_{1/2},Zn,Va)_2(Cu,Va)_1(S)_1$ for diginite, $(Co,Cu,Fe,Ni,Va)_2(S,Va)_2$ for Ni_3S_2, $(Co,Cu,Fe,Ni)_1(S)_2$ for pyrite, as well as $(Co,Cu,Fe,Ni,Va)_1(S)_1$ for pyrrhotite solid solution phases where Va is vacancy. Austenite or FCC_A1 solid alloy has a description of a substitutional solid solution, equal to sublattice structure $(Co,Cu,Fe,Ni,S)_1(Va)_1$.

The following principal calculations were performed during systematic determination of equilibrium cooling characteristics for respective matte systems. Liquidus equilibria were calculated for the Cu–Ni–S ternary system in the context of variable iron endpoint concentrations. The Cu and Ni corners were treated as mixtures of chemical elements and composite purposely with iron concentrations of 5%, 1% and 0.1% for respective systems. All percentages used in ternary constitution are in weight% unless specifically otherwise acknowledged. The upper and lower temperature limits were set to 1423 K (1150 °C) and 923 K (650 °C) within the respective systems. The set temperatures were stepped using 50 K intervals and pressure was assumed at atmospheric. Further conditions and elements were set in the constitution of comparable ternary systems. Liquidus and primary phase equilibria were subsequently calculated for Cu–Ni–S ternaries including iron and cobalt concentrations. The Cu, S and Ni corners were composite with 5%Fe1%Co, 1%Fe0.5%Co and 0.2%Fe0.3%Co for respective systems. The end composition of the Cu and S corners were selected at 70% mixtures of constituent chemical elements. The upper, step and lower temperature limits were set to 1673 K (1400 °C), 25 K and 773 K (500 °C), correspondingly. Corresponding true (normalised) liquid matte starting compositions (including set iron, cobalt and oxygen concentrations) were subsequently specified and their assays were calculated as a function of liquidus equilibria. Similarly, the upper and lower temperature limits for the calculations were set to 1123 K (850 °C) and 873 K (600 °C). The set temperatures were stepped using 25 K intervals. The liquid matte starting compositions and calculated assays were superimposed on relevant Cu–Ni–S_FeCo ternary systems.

Multiphase cooling equilibria were calculated (supported by Mtox database) for the matte system Cu–Ni–S–Fe–Co–O in the context of corresponding true liquid matte starting compositions. The database contains assessed thermodynamic descriptions for the base matte system and thus allowed construction of a selection

of equilibrium features with associated compositional analysis. Upper, step and lower temperature limits were respectively set to 1773 K (1500 °C), 2.5 K and 473 K (200 °C) for these computations.

Moreover, actual features for correlated fast cooled industrial matte systems as observed by automated mineralogy, electron probe microanalysis and field emission scanning electron microscopy (FEG SEM) were incorporated and contrasted with results for the equilibrium computational approach. A FEI 600F field emission mineral liberation analyzer (FEG MLA) integrated with two liquid-nitrogen-free Bruker Xflash silicon drift detectors was made available for determination of phase modal abundance. The instrument made use of the X-ray modal abundance (XMOD) analytical routine while off-line classification was performed with reference to a compiled phase standards file. Electron probe microanalysis was performed on representative analytical samples with a Cameca SX50 microprobe equipped with four wavelength dispersive spectrometers and an energy dispersive spectrometer. The microstructure was analysed using a JEOL JSM-7001F FEG SEM employing compositional imaging and energy dispersive X-ray spectrometry (EDX)-induced phase element mapping.

3. Results and discussion

The limits of what can be achieved are set by equilibria relations while reaction kinetics and process dynamics affect the engineering of pyrometallurgical processes (Rosenqvist, 1978). It became important to develop a fundamental understanding of liquidus and phase equilibria relations for Cu–Ni–S ternary systems as an approximation of nickel converter matte composition. Multi-component systems were build-up progressively from simpler systems to ensure relevance to industrial matte systems.

3.1. Liquidus equilibria

Fig. 1 illustrates the calculated liquidus temperature range plotted as isothermal contours for iron endpoint related Cu–Ni–S ternary systems. The Cu and Ni end member components (which assist in defining the system) are mixed with iron to include the effect on the calculations. Iron decreases to zero as the composition and sulphur shift to the pure S-apex.

Fig. 1a indicates that liquid phase would be stable from 1373 K (1100 °C) to 973 K (700 °C). Isothermal contours (annotated by numeric values) fall away from the Cu5Fe and Ni5Fe corners as well as along the upper Ni5Fe–S join. Note in particular the direction of falling isothermal contours from Cu5Fe corner towards a liquidus valley near the lower Ni5Fe–S join. Fig. 1a also provides an impression of a liquidus valley near the lower Cu5Fe–S join. Similarly, examination of Fig. 1b reveals the stabilization of liquid phase from 1373 K to 973 K and a liquidus valley facing the lower Ni0.1Fe–S join. Fig. 1b also presents an impression of a flatter liquidus valley near the centre of ternary system. Comparative liquidus equilibria results (not shown here) to that presented in Fig. 1b were obtained for the Cu1%Fe–Ni1%Fe–S ternary system. The results in general can be cautiously applied in showing the effect of ternary constitution on the stable liquidus temperature range. Liquid phase has not been stable at the preset lower temperature of 923 K (650 °C). The lower liquidus temperature range of all systems is therefore below 973 K but above 923 K. The value of preset temperature intervals may not be small enough to detect the lowest liquidus temperature range for the respective ternary systems.

3.2. Ternary and liquid phase equilibria

Fig. 2 illustrates the calculated liquidus temperature range plotted as isothermal contours for the Cu–Ni–S_5%Fe1%Co ternary