

**Phase relations in the system
Cu-Fe-Ni-S and their application
to the slow cooling of PGE**

Matte

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ABBREVIATIONS

°C	degrees Celsius
ci	confidence interval
EMP	Electron Microprobe
E1,2,3	Eutectic point 1,2,3
Fig.	Figure
Glass	quartz glass
Heaz. / Hz	Heazlewoodite
kV	kilo Volts
µm	micro meter
nm	nano meter
nA	nano Ampere
No. Anal.	Number of analyses
PGE	Platinum Group Element
PGM	Platinum Group Mineral
s	standard deviation
Std. Dev.	Standard deviation
UG2	Upper Group (layer) 2
wt%	weight percentage
at%	atomic percentage

ABBREVIATIONS FROM BRUWER (1996) FOR ISOTHERMAL SECTIONS IN THE Cu-Ni-S SYSTEM

L ₁	Sulphur liquid containing approximately 1 wt% Cu and Ni
L ₂	Immiscible Cu-rich sulphide liquid
L ₃	Immiscible metal-rich liquid
L _(2,3)	Homogeneous liquid field forming an eutectic at approximately 575°C
L ₄	Liquid field that separates from the L _(2,3) field and exists around 800°C
µ	High temperature Digenite (Cu _{2-x} S)
θ	High temperature Heazlewoodite (Ni _{3±x} S ₂)
λ	High temperature Millenite (Ni _{1-x} S)
η	Vaesite (NiS ₂)
α	Cu-Ni alloy
+	Phase assemblages are noted with a "+" between co-existing phases, refers to the field where these phases co-exist

ABSTRACT

The aim of this investigation is to determine the influence of a small amount of Fe on the Cu-Ni-S system within the framework of the beneficiation processes of Platinum Group Metals from the Merensky Reef of the Bushveld Complex, South Africa. Aspects under evaluation are: the phase relations within the Cu-Ni-Fe-S system at less than 10 wt% Fe, the difference in cooling paths as the Fe content and temperature vary, and the variation in composition of the phases that form between 1200° and 700°C.

The investigation was performed in 100°C intervals from 1200°C to 700°C at four different Fe contents (i.e. 1, 3, 5 and 10 wt%). High purity metal and sulphur powders were reduced and dried respectively and experiments were carried out in evacuated quartz glass tubes. Modified high-temperature furnaces with an accuracy of 1°C were used for equilibration reactions, which lasted between a few hours (at 1200°C and 1100°C) up to a couple of months (at 800°C and 700°C). Experiments were quenched in tap water to preserve the phase relations at the required temperature. Electron microprobe analyses were collected to determine the chemical composition of solid and quenched melt phases. Spot analyses were performed on the solid phases and area analyses, using the defocused beam technique, to determine the average composition of the quenched melt phases. Results were plotted on a quaternary diagram and projections onto the Cu-Ni-S ternary diagram were used to compare between diagrams with different starting Fe contents. Diagrams at similar starting Fe contents and different temperatures were combined to produce diagrams depicting the cooling path from 1200°C to 700°C (the paths to complete solidification were extrapolated).

Alloy is the first phase to crystallize in an average converter matte (provided the composition is favorable) and also the primary collector of PGE's in the matte. In this investigation it was confirmed that at a fixed bulk Fe content, a decrease in temperature causes a decrease in the Cu/Ni of the cotectic alloy. Additionally, it has also been established that at a fixed temperature, an increase in the Fe content of the bulk will cause a decrease in the Cu/Ni of the cotectic alloy. Therefore, if all other parameters are kept stable, it can reasonably be accepted that an increase in the bulk Fe content will produce an increasingly Ni-rich alloy.

The composition of the cotectic melt is essential in determining the cooling path towards the eutectic point where alloy, digenite and heazlewoodite coexist. The cotectic melt in the assemblage (alloy+digenite+melt) shows an increase in Ni, Fe and sulphur content, with an increasing Fe content in the bulk. This causes the cotectic to shift towards higher sulphur contents, which results in a larger stability field for alloy. The implications are twofold: Firstly higher Fe contents increase the amount of alloy that will crystallize from the melt, and secondly it would require a larger variation in starting composition (particular the Cu/Ni) to alter the path of crystallization of a matte.

The stable phases are strongly influenced by the amount of Fe present in the bulk composition: The more Fe available, the more Fe will be incorporated in the crystal structures of phases. The relationship is, however, not linear and generally the more Fe available in the bulk the wider the range of Fe contents in the phase. In assemblages containing alloy, the alloy phase has consistently the highest partitioning coefficient for Fe. In other assemblages, Fe does not show any preference for a particular phase, regardless of the sequence of crystallization or temperature of equilibration.

PREAMBLE

The definition given by Collins (1990) for a mineral is: "a naturally occurring element or compound of non-biological origin, having an ordered atomic structure and characteristic chemical composition, physical properties, and crystal form". Although the phases (e.g. "digenite", "millerite", "vaesite" and "covellite") in the Cu-Ni-Fe-S system from this investigation might show the same structure and characteristics as the natural occurring minerals, they can not, in the strict sense of the word, be classified as minerals. The sulphide phases in the various sub-systems (Chapter 2) and those from this investigation are all synthetic sulphides. However, because there is no referral to the natural minerals themselves, the sulphides in this investigation will be named by their natural equivalents with the understanding that they are all synthetic.