

2. THE FeO-TiO₂ SYSTEM

The section below outlines the earlier work done on the FeO-TiO₂ system. During ilmenite smelting operations an equivalent of TiO₂ content of 85% or higher and a FeO content of approximately 10% are typical. Earlier results on phase relations in the FeO-TiO₂ binary system are not consistent, nor are they clearly defined for slag containing 80% TiO₂ and higher. The initially reported phase diagram of the binary system FeO-TiO₂ (Grieve & White, 1939), indicated two stoichiometric compounds: ulvospinel (2FeO.TiO₂) incorrectly named pseudobrookite, and ilmenite (FeO.TiO₂), Figure 8.

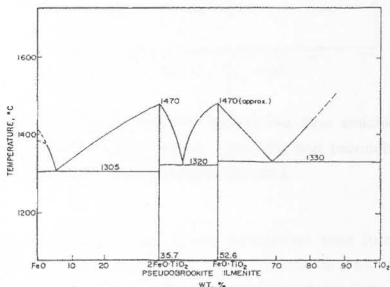


Figure 8: Phase relations in the system FeO-TiO₂ (Grieve & White, 1939). The two stoichiometric compounds present are ulvospinel (incorrectly named pseudobrookite) and ilmenite.

The usage of a Tungsten-molybdenum thermocouples which are prone to oxidising, gave rise to erroneous temperature measurements. The erroneous reported phase equilibria are therefore attributed to the presence of Fe⁺³ cations on the FeO-rich side and the Ti⁺³ cations on the TiO₂ rich side (a result of the oxygen partial pressure) and an incorrect temperature range and possible erroneous temperature measurements due to oxidation of the thermocouples (Brauer & Littke, 1961).

MacChesney and Muan (1961) conducted experimental work in an atmosphere defined by the Fe/FeO atmosphere. Pseudobrookite was reported to melt isothermally with a eutectic at approximately 80%TiO₂.

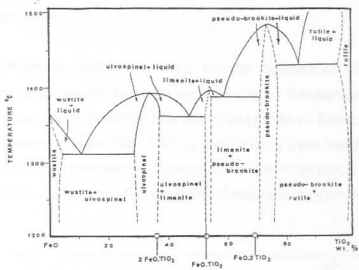


Figure 9:Phase relations in the FeO-TiO₂ system. The three stoichiometric compounds ulvospinel (2FeO.TiO₂), ilmenite (FeO.TiO₂) and pseudobrookite (FeO.2TiO₂) were identified (McChesney and Muan, 1961).

Attempts to melt FeO-TiO₂ slags of various compositions were successful only for slag containing less than 62% TiO₂ (Smith & Bell, 1970). The absence of the eutectic temperature at 1430°C at approximately 80% (Figure 9) was confirmed by Grau (1979) (Figure 10). Pseudobrookite is reported to melt incongruently.

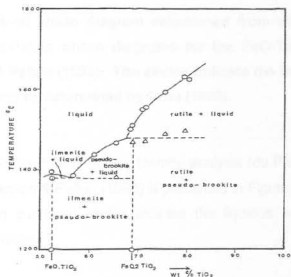


Figure 10:Phase relations in the FeO-TiO₂ system for the TiO₂ rich side (Grau, 1979).

An optimised phase diagram from all available thermodynamic data and existing phase diagrams for the FeO-TiO₂ system was reported by Eriksson and Pelton (1993). This corresponded to that of MacChesney and Muan at high FeO concentrations and to that of Grau at high TiO₂ concentrations.

A modified quasichemical model was used for the optimisation in which all available thermodynamic and phase equilibrium data were calculated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. The compounds Fe₂TiO₄, FeTiO₃ and FeTi₂O₅ were treated as stoichiometric in the optimisations since their stoichiometric ranges of several mole percentage are due to mixed oxidation states of iron and titanium. The maximum inaccuracy is estimated to be approximately 20 °C.

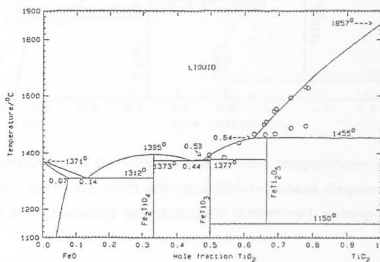


Figure 11: An optimised phase diagram determined from all available thermodynamic data and existing phase diagrams for the FeO-TiO₂ system as reported by Eriksson & Pelton (1993). The circles indicate the liquidus curve and peritectic temperatures as determined by Grau (1979).

A comparison of results as determined by thermal analysis (du Plooy, 1997) with the optimised phase diagram by Eriksson & Pelton (1993) is presented in Figure 12: Filled circles indicate the thermal analyses and the open circles indicate the liquidus and solidus temperatures as determined by Grau (1979).

The results obtained by du Plooy (1997) agreed well with those of Grau (1979) on which the optimised phase diagram was based by Eriksson & Pelton (1993). The results were within 40 °C of the reported liquidus and solidus temperatures, except for the liquidus temperatures at

0.47 and 0.58 mole fraction TiO_2 . The absence of the eutectic just above 80 wt% TiO_2 can be seen again.

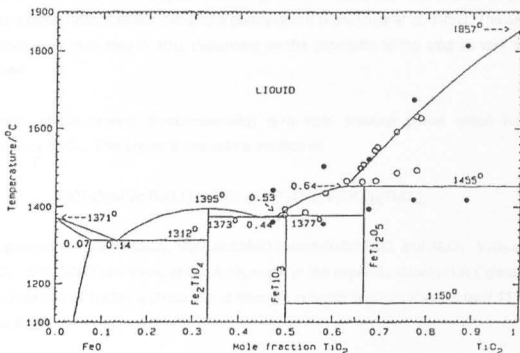


Figure 12:A comparison of the liquidus and solidus temperatures obtained by thermal analysis (du Plooy, 1997) with the optimised phase diagram (Eriksson & Pelton, 1993) and previously experimentally determined melting points (Grau, 1978)