3. PHASES IN SOLIDIFIED HIGH TITANIA SLAGS

There are four main mineralogical phases present in solidified high titania slags namely psuedobrookite, rutile, metallic iron and a glassy phase (Bessinger et al. 1997). The amounts of the phases vary from slag to slag, depending on the chemistry of the slag as well as cooling conditions.

The major phase present (pseudobrookite) is a solid solution phase which follows the stoichiometry M_3O_5. This phase is basically a solution of:

$$(FeTi_2O_5)a(MgTi_2O_5)_b(Al_2TiO_5)_c(MnTi_2O_5)_d(V_2TiO_5)_e(Ti_3O_5)_g$$

As this general formula indicates, MgO and MnO substitute for FeO, and Al_2O_3 , V_2O_3 and Cr_2O_3 for Ti_2O_3. SiO_2, CaO and some of the Al_2O_3 occur in the separate silicate-rich ("glass") phase. The FeO content of the M_3O_5 phase varies from 2% in highly reduced slags to over 11% for less reduced slags.

Another prevalent phase is rutile. The rutile phase shows some solubility of FeO, and to a minor extent of MnO. The other phases present are a metallic and glass phase. The glass phase mainly consists of SiO_2, TiO_2, FeO, CaO and Al_2O_3. Figure 13 below shows the glass phase along the edge of the dominant M_3O_5 phase, with small amount of metallic iron in between.

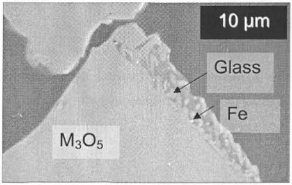

Figure 13:Structure of titania slag (le Roux, 2001)

Pistorius (2002) investigated the relationship between FeO and Ti_2O_3 and came to the conclusion that this slag composition follows a set relationship. It was concluded that this could be attributed to a phase chemistry effect and not an equilibrium or kinetic effect. The effect of impurities on the FeO-TiO_2 relationship was also investigated. The impurity content of the ilmenite fixes the impurity content of the slag as well as the FeO-Ti_2O_3 relationship (Figure 14). Figures 15 and 16 below show that the slag composition does correspond well to stoichiometric M_3O_5 when impurities are taken into account.

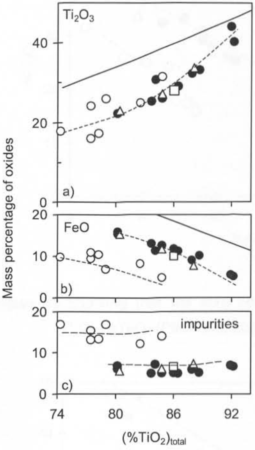

Figure 14: Changes in FeO, Ti_2O_3 and impurity oxide content with increased equivalent total TiO_2 content, for slag produced from Canadian ilmenite (open circles) and South African ilmenite (others) (Symbols: • Iscor pilot plant, Δ Richards Bay Minerals, □ Namakwa Sands). Solid lines in a) and b) given calculated relationship for pure FeO-Ti_2O_3-TiO_2 slag in equilibrium with pure liquid iron at 1650°C. (Pistorius, 2002)

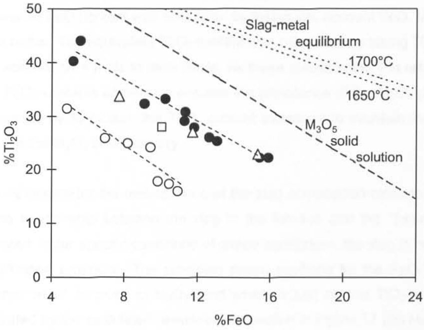

Figure 15:Showing that the slag composition does not correspond to stoichiometric Ti_3O_5-$FeTi_2O_5$ (Pistorius, 2002).

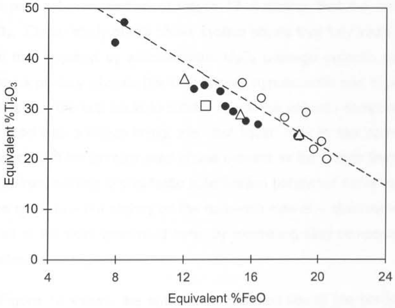

Figure 16:Showing that the slag composition corresponds well to the stoichiometric M_3O_5 when impurities are taken into account.

The effect of impurities was determined by calculating the equivalent FeO and Ti_2O_3. The equivalent FeO content was calculated by taking into account FeO, MgO and MnO on a mole to mole basis. The equivalent Ti_2O_3 content was calculated by taking Ti_2O_3, Cr_2O_3, V_2O_3 and Al_2O_3 into account on a mole to mole basis. As these results show, the relationship between the FeO and Ti_2O_3 contents of the slag ensures the prevalence of the M_3O_5 phase. As the FeO content is lowered by reduction, the Ti_2O_3 content increases to maintain the overall slag composition close to the M_3O_5 stoichiometry.

A likely reason for the maintenance of the slag composition close to stoichiometric M_3O_5 is the phase relationship between the slag in the furnace and the "freeze lining". The furnace is operated under specific conditions of phase equilibrium, the slag is held in near equilibrium with solidification products. The predicted phase equilibria for the FeO-Ti_2O_3-TiO_2 system show a eutectic which is close to M_3O_5 (and which is just on the TiO_2-rich side of M_3O_5). This is illustrated by the calculated pseudobinary section in Figure 17 (no Magnéli phases considered). Data for the FeO-TiO_2 and TiO_2-Ti_2O_3 binary systems with their extension to the ternary system FeO-TiO_2-Ti_2O_3 were used in FactSage to perform equilibrium calculations (see section 4 for a brief discussion of FACTSage). Impurities present in the slag were also taken into account as discussed in the previous paragraph.

The pseudobinary section of Figure 17 illustrates that the eutectic composition lies close to M_3O_5. Closer study of this phase system shows that fully liquid slags with TiO_2 contents higher than that required by stoichiometric M_3O_5 undergo eutectic solidfication, with either M_3O_5 or rutile as primary phases (for respectively hypoeutectic and hypereutectic TiO_2 contents). This means that the last liquid to solidify lies at the eutectic composition. Given that the furnace is operated with a freeze lining, this "last liquid" may in fact correspond to the liquid slag in the furnace, with the primary solid phase present as the freeze lining. In this way, the combination of the freeze lining and eutectic solidification behaviour serve to constrain the slag composition to be close to – but slightly on the rutile-rich side of – stoichiometric M_3O_5. This prediction was tested in the work presented here, by examining slag compositions from a pilot-scale ilmenite smelter.

As Figure 17 shows, the eutectic composition lies at the border between the M_3O_5 and rutile primary phase fields. The predicted locations of these primary phase fields (and hence of the eutectic groove) for more widely varying slag compositions are given in Figure 19 (as determined from FACTSage). This figure illustrates that the eutectic groove is generally close to M_3O_5 (stoichiometric M_3O_5 compositions lie on the broken line which join $FeTi_2O_5$ and Ti_3O_5 in Figure 19). The samples investigated in this work are also indicated on this diagram. Their compositions are detailed in section 5.

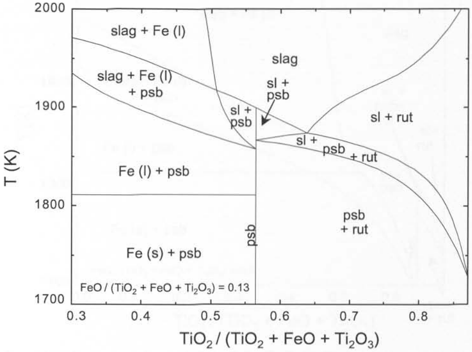

Figure 17: Calculated section through the TiO_2-Ti_2O_3-FeO phase diagram, at a constant FeO mole fraction of 0.13 (corresponding to a low-FeO smelter slag). Magnéli phases were not considered in the calculation. Phases are identified as follows: "sl" is the molten oxide (slag), "psb" is the M_3O_5 phase, "rut" is the rutile-based solid solution (TiO_2 with some Ti_2O_3 in solution), and "Fe" is metallic iron

For samples with a higher FeO content (as shown in Figure 18) pseudobrookite solidifies peritectically.

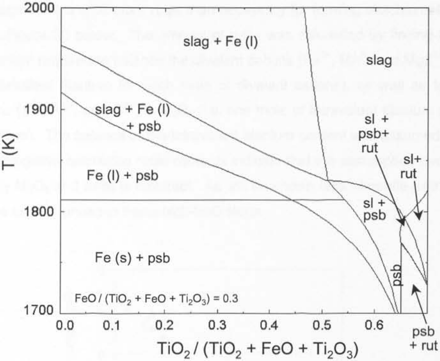

Figure 18: Calculated section through the TiO_2-Ti_2O_3-FeO phase diagram, at a constant FeO mole fraction of 0.3 (corresponding to a high-FeO slag). Phases identified as in Figure 17.

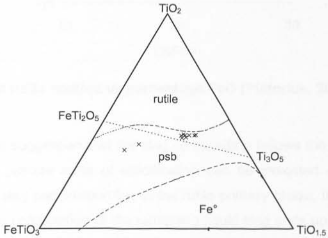

Figure 19: The ternary system FeO-TiO_2-Ti_2O_3 showing primary phase fields as predicted from calculations with FACTSage. "Fe°" is metallic iron and "psb" is M_3O_5. Compositions plotted on a molar basis.

The aim of this discussion is to test whether the liquid slag in the furnace does follow the eutectic composition. Below the samples used during the investigation are plotted in terms of the calculated rutile content vs the percentage FeO. It can be seen that besides the samples with a high FeO content most samples lie in the region above the stoichiometric M_3O_5. Thus most of the slags contain a bit more rutile than necessary for forming stoichiometric M_3O_5. This is indicated in Figure 20 below. The amount of rutile was calculated by finding the amount of tetravalent titanium required to balance the divalent cations (Fe^{2+}, Mn^{2+} and $Mg2^{2+}$) in M_3O_5 (i.e. two moles tetravalent titanium for each mole of divalent cations), as well as to balance the trivalent cations (V^{3+}, Al^{3+}, and Ti^{3+}) in M_3O_5 (i.e. one mole of tetravalent titanium per two moles of trivalent cations). The balance of the tetravalent titanium content was assumed to be present as free rutile. Negative calculated rutile contents indicate that the assumption that the structure consists of only M_3O_5 and rutile is incorrect. As will be shown later, ilmenite (rather than rutile) was present as second phase in these high-FeO slags.

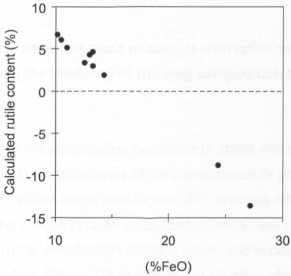

Figure 20: Calculated rutile content vs percentage FeO (Pistorius, 2002)

In order to support the suggestion that the slag composition follows the eutectic groove on the liquidus diagram, the precise route of solidification can be indicated on the FeO-TiO_2-Ti_2O_3 ternary system. If the slag composition lies in the rutile primary phase, it can be seen that after partial solidification the composition of the remaining liquid slag ends up on the eutectic groove as illustrated below in Figure 21 (as determined from FACTSage). For the slag with rutile as primary phase a slag with a composition of 13.6% FeO, 27.4% Ti_2O_3 and 59% TiO_2 (mass basis) was chosen. The sample with pseudobrookite as primary phase had a composition of approximately 10% FeO, 49% TiO2 and 41% Ti_2O_3 (mass basis).

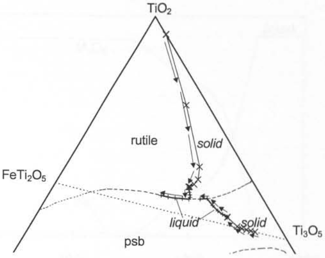

Figure 21: Predicted solidification route of sample with rutile and psuedobrookite primary phases showing the tendency of the slag composition to end up on the eutectic groove.

It is interesting to note that the solidification behaviour of titania slags is quite unique compared to other slags. In addition to the dominance of the pseudobrookite phase, high-titania slags have a very narrow solidification range (see Figure 23), whereas other slags, for example steelmaking slags, exhibit a much broader solidification range (see Figure 24). For high-FeO slags (Figures 22a and b) the solidification range is wider, and either metallic iron or illuminate forms upon final solidification. Figure 22a illustrates the situation where Fe formation is allowed. If Fe formation is suppressed ilmenite will form as illustrated in Figure 22b.

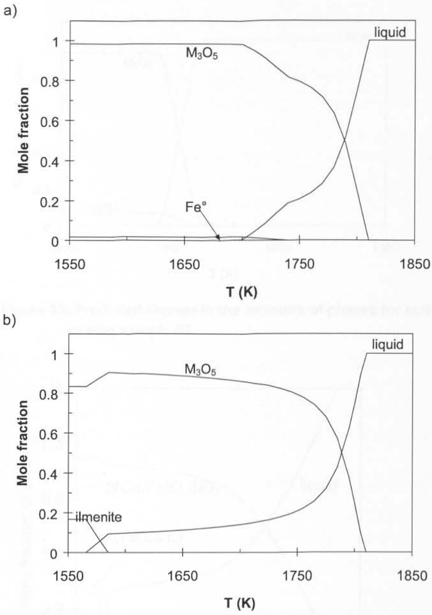

Figure 22: Predicted change in the amounts of phases for solidification of slag sample 10
a) Fe formation allowed
b) Fe formation suppressed

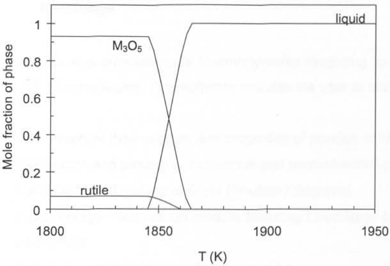

Figure 23: Predicted change in the amounts of phases for solidification of slag sample 83

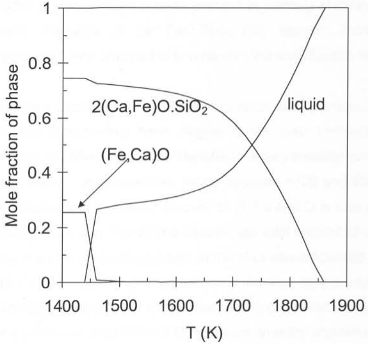

Figure 24: Predicted change in the amounts of phases for solidification of a typical steelmaking slag with composition 30%FeO, 20%SiO_2, 50%CaO (mass basis). This illustrates the broad solidification range of the slag as compared to the narrower solidification range of typical titania slags.