Equilibrium interactions between freeze lining and slag in ilmenite smelting

by P.C. Pistorius*

Synopsis

In ilmenite smelting, the FeO content of the feed material (nominally FeO·TiO2) is decreased by reduction with carbon. In a parallel reaction, a significant amount of the TiO2 is reduced to Ti3O5. One of the striking features of these reactions is a consistent relationship between the extents of FeO and TiO2 reduction; this relationship is independent of furnace size. It was recently proposed that this relationship follows from the solidification behaviour of the slag, where the final slag composition corresponds to the minimum melting point (‘eutectic groove’) in the FeO-TiO2-Ti3O5 phase system; the hypothesis is that solidification equilibrium with the freeze lining stabilizes the slag composition. If this is the case, the system of slag and freeze lining must be capable of correcting two types of disturbances: thermal and compositional. Thermal disturbances result from incorrect power input, for the feed rates of ilmenite and reductant. For example, excessive power input will tend to overheat the slag, causing the freeze lining to melt partially, establishing a new steady-state heat loss from the furnace. Compositional disturbances result from an incorrect reductant input for the given power and ilmenite input. In this work, the dynamic response of the slag and freeze lining to different inputs (flow rates of ilmenite and reductant, and power input) is modelled. The model is based on solidification equilibria, and quantified heat loss through the freeze lining. The conclusion is that the solidification equilibrium cannot constrain the composition to the eutectic groove for typical operating conditions.

Keywords: ilmenite smelting, freeze lining, solidification, high-titanium slag

Background

Ilmenite smelting is one of the methods to upgrade the iron-titanium oxide mineral ilmenite to a high-titanium feedstock for rutile pigment manufacture. The product of ilmenite smelting is a high-titanium slag, which typically contains around 9% FeO, 50% TiO2, and 35% Ti3O5, with the balance being other impurity oxides. This slag is corrosive to refractory materials, and hence a layer of solidified slag is used as a ‘freeze lining’ on the furnace sidewalls.

The freeze lining hence plays an essential role in protecting the furnace lining. It has recently been suggested that the interplay between the solidified freeze lining and the liquid slag also affects the composition of the liquid slag: a line of minimum melting points (a ‘eutectic groove’) was found to separate the primary phase fields of rutile (TiO2) and pseudobrookite (M3O5, a solid-solution phase, which is a combination of FeTi2O5 and Ti3O5 in the three-component system FeO·TiO2-Ti3O5). It was suggested that the solidification equilibrium forces the liquid slag composition to lie along the eutectic groove. This suggestion offers a possible explanation for the remarkable constancy of the phase composition of solidified titania slag (this constancy is that solidified slag consists mainly of M3O5 and a few per cent of rutile, with the minor components SiO2 and CaO in separate phases; the dominance of the M3O5 phase persists over a wide range of FeO contents). As Figure 1 indicates, the eutectic groove lies between the M3O5 and rutile compositions, which means that slags with compositions along the groove solidify as a mixture of M3O5 and rutile. (The predicted phase diagram does indicate a larger fraction of rutile in solidified slags than found in practice—for example, a slag with 10% FeO [mass basis] and which lies on the eutectic groove is predicted to contain 18% rutile after solidification, about three times the actual amount.)

In the work presented here, the suggestion—that interaction with the freeze lining serves to stabilize the slag composition along the eutectic groove—is tested by using solidification equilibrium data (ternary phase diagrams for the FeO·TiO2-Ti3O5 system), and a simple heat transfer model. This model was used to test the sensitivity of the slag composition to thermal and compositional perturbations.

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In the following section, the relevant equilibrium data are summarized first; the model description and model results then follow.

Equilibrium data

Calculation procedure

The phase diagram data were calculated by using the FACTSage® software, using the quasichemical model for the liquid slag and near-ideal solid solution in M3O5 as described before, and considering rutile as pure TiO2 (i.e. neglecting the small solubility of Ti2O3 in rutile). Magnéli phases were also not considered, for the reason that solidified slag has not been found to contain these phases (although thermodynamic calculations indicate that they should form). Compositions lying between M3O5 and TiO2 were considered, since this is the range of actual tap compositions. In the phase diagrams shown in Figure 1 and later figures, the end species are taken as TiO2 (rutile), Fe1/3Ti2/3O5/3 (ferrous pseudobrookite, normally written as FeTi2O5, but shown here as the species containing 1 cation per formula unit), and TiO5/3 (anosovite, normally written as Ti3O5). (For the single-cation forms of the end species chosen here, mole fractions are nearly equal to mass percentages.)

For speed of calculation in the heat transfer model, the phase equilibrium data generated with FACTSage® were represented by a series of polynomial expressions, which describe the shapes of the liquid/(rutile + liquid) phase boundary and the liquid/(pseudobrookite + liquid) phase boundary, and the dependence of the slopes of the pseudobrookite-liquid tie lines on pseudobrookite composition. Different polynomials were fitted to phase boundaries for temperatures from 1815K to 1895K, at intervals of 10K; as Figure 2 indicates, the range from 1815K to 1895K spans the liquidus temperatures of slags which lie along the eutectic groove, with FeO contents ranging from as little as 1.5% to 22%.

With these data on phase equilibria, a program was written (in Visual Basic) to calculate the equilibrium phase composition (amounts of phases, and composition of each phase, at a given temperature and overall composition), for slags in the TiO2-Fe1/3Ti2/3O5/3-TiO5/3 system. The enthalpy of the phase mixture was found by adding the contributions of each phase to the overall enthalpy of the mixture, according to the compositions and enthalpy values of each phase. Simplified expressions were fitted to the enthalpy data; these expressions are listed in Tables I and II.

Table I

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
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<tbody>
<tr>
<td>TiO2</td>
<td>-966.552</td>
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<tr>
<td>Ti3O5</td>
<td>-2945.862</td>
<td>158.0</td>
<td>0.02511</td>
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<td>FeTi2O5</td>
<td>-2212.171</td>
<td>164.1</td>
<td>0.01140</td>
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Table II

<table>
<thead>
<tr>
<th>Constant</th>
<th>(d_{\text{FeO}})</th>
<th>(d_{\text{TiO1.5}})</th>
<th>(d_{\text{TiO2}})</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value (kJ/g-atom)</td>
<td>-236.3</td>
<td>-106.8</td>
<td>-257</td>
<td>0.0275</td>
</tr>
<tr>
<td>Units</td>
<td>kJ/g-atom</td>
<td>kJ/g-atom</td>
<td>kJ/g-atom</td>
<td>kJ/g-atom.K</td>
</tr>
</tbody>
</table>

Figure 1— Isothermal section through part of the TiO2-FeO-Ti2O3 system, at 1875 K. The base of the diagram represents the M3O5 solid solutions, between ferrous pseudobrookite (here shown as Fe1/3Ti2/3O5/3) and anosovite (shown as TiO5/3). Diagonal broken lines indicate compositions of constant FeO content, on a mass basis, of respectively 5, 10, 15, 20 and 25%. Some tie lines are shown in the dual-phase regions. The curved broken line from lower left to right is the ‘eutectic groove’ which separates the rutile and pseudobrookite primary phase fields. Diagram is calculated on the basis of curve-fits to equilibrium data taken from FACTSage.

Figure 2— Extent of fully liquid region in the TiO2-Fe1/3Ti2/3O5/3-TiO5/3 system, for temperatures from 1815K to 1895K. Diagonal broken lines indicate compositions of constant FeO content, on a mass basis, of respectively 5, 10, 15, 20 and 25%. The curved broken line from lower left to right is the ‘eutectic groove’ which separates the rutile and pseudobrookite primary phase fields. Diagram calculated on the basis of curve-fits to equilibrium data taken from FACTSage.
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**Solidification behaviour: heat of solidification and solidification range**

Two prominent features of solidification in this system are worth emphasizing; these features have strong effects on the freeze lining behaviour. These two features are the narrow solidification range, and the large heat of solidification compared with the heat capacity of the liquid and solid phases; both features are illustrated by Figure 3 (a) and (b). This figure plots the calculated enthalpy of three mixtures which contain 10% FeO by mass, but which lie at different locations relative to the eutectic groove – to give respectively rutile, pseudobrookite, and a combination of both, as primary phases. Note that the enthalpy values are given in joule per g-atom, where 'g-atom' indicates the number of moles of atoms (Fe, Ti and O) in the mixture. The large vertical steps in the enthalpy plots, in the range 1840–1890K, indicate the solid-liquid transition. In each case, the transition occurs over a narrow temperature interval of – at most – 30K. The heat of solidification is more than 17 kJ/g-atom in all three cases. Comparison with the heat capacity of the molten slag of 0.0275 kJ/g-atom (see Table II) reveals that solidification causes as large an enthalpy change as would a temperature change, in the case of fully liquid slag, of more than 600 K.

**Heat transfer and energy balance model**

An approximate one-dimensional pseudo-steady-state heat transfer calculation was used here; its main features are illustrated by Figure 4. The rate of heat transfer through the furnace lining was calculated from the series resistances through the freeze lining and the furnace wall. In both cases, the resistance is calculated from the following relationship:

\[
R_{\text{conduction}} = \frac{\ln\left(\frac{r_{\text{outer}}}{r_{\text{inner}}}\right)}{(2\pi k h)}
\]

where \( r_{\text{outer}} \) and \( r_{\text{inner}} \) are the radii at the outside and inside of the conductor, \( k \) is its thermal conductivity, and \( h \) is the height of the conductor (which is the depth of the slag bath; see Figure 4). It was assumed that the resistances at the resistances at the outside of the furnace lining (i.e. through the steel shell, and conduction to the cooling water) are negligible. The rate of heat loss through the furnace wall is hence given by:

\[
q_{\text{side}} = \frac{(T_{\text{slag}} - T_{\text{water}})}{(R_{\text{freeze}} + R_{\text{refractory}})}
\]

where \( T_{\text{slag}} \) is the temperature of the slag and freeze lining in the furnace, \( T_{\text{water}} \) is the temperature of the cooling water, \( R_{\text{freeze}} \) is the conduction resistance through the freeze lining, and \( R_{\text{refractory}} \) is the conduction resistance through the refractory.

Values of the constants used in this model are given in Table III. As these values show, the physical size of the modelled furnace corresponds to a pilot-scale furnace. This size of furnace was chosen for several reasons: the availability of data for this furnace, the large wall contact area relative to slag volume (which will tend to emphasize any freeze lining effect), and the observation that the compositional relationships in these slags do not depend on furnace design (i.e. any effect which controls the relationship between FeO and TiO\(_2\) must also apply to the pilot-scale furnace).

Together with the conduction heat transfer calculation, the energy balance included the effects of feeding slag into the slag bath, and of applying power (by arcing) to the bath. The slag fed to the bath was specified by its molar flow rate, its composition, and its temperature. In specifying the feed to...
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the bath as slag (rather than ilmenite and carbon) the details of the chemical reaction were not considered. The slag flow and current furnace contents were inputs to the mass balance: after each time interval, the amounts of FeO, TiO₂ and Ti₂O₅ in the furnace were recalculated, from the amount which had been in the furnace at the start of the time interval, and the amount that entered in the slag feed during the interval. In performing this mass balance, no chemical reaction subsequent to the initial reduction of the ilmenite was assumed to take place (i.e. no redistribution of oxygen between iron and titanium was allowed). The energy balance was performed similarly, by finding the total enthalpy of the bath from the enthalpy of the slag bath at the start of each time interval, the enthalpy of the slag which was fed, heat lost through the furnace wall (Equation [2]), and power input from the arc. From the energy balance and mass balance, the molar enthalpy and average composition of the furnace at the end of the time interval was known. This was then used to find the furnace temperature from the calculated dependence of enthalpy on temperature for the specific composition (i.e. using data such as shown in Figure 3). A simple interpo-lation procedure was used to determine temperature from enthalpy.

From the new furnace temperature and slag composition, the fraction of solid material was calculated (with the phase diagram information); this was then used to find the new thickness of the freeze lining. In this calculation, it was assumed that the molar densities of the freeze lining and liquid slag are equal (with the value as given in Table III). The new depth of the slag bath was similarly found from the mass balance (the total number of moles of material, whether solid or liquid, in the furnace), the internal diameter of the furnace, and the molar density.

This simplified approach neglects many of the complexities which arise in actual furnaces. Here, the freeze lining is assumed to be in full equilibrium with the liquid slag, with the possibility to change its composition within one time step. In reality, at most limited diffusion will occur within the solid lining. Also, temperature differences within the liquid slag are neglected, as are two-dimensional heat transfer (to the furnace roof above, and the metal bath below), and the details of chemical reaction kinetics. Most of these effects are incorporated in a much more detailed model which is being developed. However, this simplified model already offers useful insights, as discussed below.

Results and discussion

The results presented below refer to the pilot-scale furnace as discussed earlier. For this furnace, the typical maximum power input into the bath (excluding heat losses to the roof) is some 1 MW, with an ilmenite feeding rate of up to 1 ton/h. This typically resulted in the bath depth increasing by 0.5 m over 5 hours (corresponding to a slag mass increase of approximately 3 tons).

For each slag production rate and slag composition, the required power and reductant inputs were calculated from a simple mass and energy balance. In this calculation, it was assumed that the slag, CO, and liquid iron (with 2% C in solution) are produced at the stated feed temperature of the slag. The enthalpy data as listed in Table II were used for the liquid slag, with other values taken from literature compilations. The feed material was assumed to be stoichiometric ilmenite (FeTiO₃) and pure carbon, at 298 K.

**Freeze lining stability**

In furnaces of this type, accurate control of the mass and energy balance is crucial, because producing the slag requires a specific balance of reductant and power input. Disturbing this balance can cause loss (melting) of the freeze lining, or solidification of the furnace contents. Hence supplying electrical power without feeding ilmenite and reductant is inherently dangerous. This is illustrated by Figure 5, which shows the effect on the freeze lining thickness of maintaining the power input at 1 MW (without any feed), when the bath is 0.5 m deep. This calculation is for a thick initial freeze lining, of 0.13 m (solids fraction 27% of furnace contents). Even with this thick lining, the lining is lost after 15 minutes of power input (beyond which time attack of the refractory lining will start). The effect of the heat of solidification to maintain the furnace temperature at a nearly constant value is also evident in Figure 5 (a); note the rapid heating once the freeze lining has been melted away completely. Note also the very low rate at which the freeze lining grows (and the furnace contents cool down) if no power is input (Figure 5 (b)). This emphasizes that, while the freeze lining can be melted away rapidly, regrowth of the lining is a much slower process. (Slightly faster solidification than that shown in Figure 5 (b) will be found in practice, because of additional heat loss to the furnace roof and metal bath.)

These effects can be understood in quantitative terms by noting that the heat of solidification of 17 kJ/g-atom is equivalent to 57 kJ/mol (where the slag species considered are FeO, TiO₂, and Ti₂O₅), or 2.3 GJ/m³. With 27% of solids in the furnace, and a total bath depth of 0.5 m, the volume of solids is 0.34 m³, which requires some 776 MJ to melt. If the total 1 MW of power input goes towards melting the freeze lining, total melting is hence expected to take only 776 s. The actual time is about 15% longer than this, reflecting the comparatively small effect of heat losses through the furnace lining; with no freeze lining, the heat loss by conduction through the furnace wall (per unit depth of slag) is some 200 kW/m.

In contrast with this, if the freeze lining is 0.13 m thick, the rate of heat loss through the furnace wall is only some 48 kW/m, corresponding to a rate of solidification of the lining of some 15 mm/h.

<table>
<thead>
<tr>
<th>Table III</th>
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<tbody>
<tr>
<td><strong>Constants used in heat transfer model</strong></td>
</tr>
<tr>
<td>Cooling water temperature (K)</td>
</tr>
<tr>
<td>Thermal conductivity of refractory (W/mK)</td>
</tr>
<tr>
<td>Thermal conductivity of freeze lining (W/mK)</td>
</tr>
<tr>
<td>Outer radius of refractory (m)</td>
</tr>
<tr>
<td>Inner radius of refractory (m)</td>
</tr>
<tr>
<td>Initial slag bath depth (m)</td>
</tr>
<tr>
<td>Molar density of slag and freeze (mol/m³) (Species used are FeO, TiO₂ and Ti₂O₅)</td>
</tr>
</tbody>
</table>
Slag composition response to inputs

The suggestion which is tested here is that solidification equilibrium with the freeze lining forces the slag composition to lie along the eutectic groove. The suggestion was evaluated by varying the starting compositions, initial freeze lining thickness, slag feed, slag temperature, and excess power. Two representative sets of results are shown in Figures 6 and 7. In both cases, the furnace contained material with 10% FeO by mass, but in the case of Figure 6 the starting composition lay between $M_3O_5$ and the eutectic groove, and for Figure 7 the starting composition was between the eutectic groove and rutile. In both cases, the starting temperature was selected to yield a liquid slag composition which was close to the eutectic groove; this liquid was in contact with a pseudobrookite freeze lining for the conditions of Figure 6, and with a rutile freeze lining for Figure 7. In both cases, the feed slag was chosen to contain 10% FeO, but with less TiO$_2$ (and hence more Ti$_2$O$_3$) than both starting compositions.

Two sets of results are shown for each combination, which are for different levels of excess power: zero, and 0.06 MW. The latter represents an excess of some 6%. While an apparently small percentage, this in fact is a large excess power, equivalent to superheating the liquid slag feed by nearly 400 K.

It is apparent from the results that the solidification equilibrium does not constrain the slag to the eutectic groove. In the first case (Figure 6), where both the starting and feed compositions lie between $M_3O_5$ and the eutectic groove, the liquid slag composition changes away from the eutectic groove towards the feed composition; this happens whether the freeze lining remains at approximately the same thickness (case [i]), or is melted away as a result of the excess power (case [ii]).

Where the starting and feed slag compositions are on opposite sides of the eutectic groove (Figure 7), the liquid slag composition does follow the eutectic groove for some time, for the case of zero excess power (i.e. where the freeze lining is not melted away, case [i]). However, in this case and as before, the liquid slag composition eventually departs from the eutectic groove, and changes towards the feed composition.

The conclusion from these and several other simulations (not shown here because of space limitations) is that, in contrast with the suggestion that the freeze lining can affect slag composition, the influence works in the opposite direction: changes to the inputs into the slag bath (slag composition and power) have a direct effect on the freeze lining. This result emphasizes the importance of close control of the furnace inputs, to ensure stability.
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The composition of the feed slag depends on the ratio of reductant to ilmenite, but also on the relative extents of reduction of FeO (to Fe), and of TiO₂ (to Ti₂O₃). The conclusion hence is that the inherent kinetics of these parallel reduction reactions is the likely origin of the observed slag composition relationship. Another factor is that compositional range where the slag is fully liquid is not large, at typical operating temperatures (Figure 2), with the result that liquid slag compositions cannot depart much from M₂O₅ stoichiometry.

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