1. Introduction

1.1 Ilmenite Smelting

Ilmenite smelting is a carbothermic process to upgrade the mineral ilmenite (nominally $FeTiO_3$), yielding as primary product a TiO_2-rich slag (which is mainly used as feed material for TiO_2 pigment production), and pig iron as by-product. (Khan, 1984). In ilmenite smelting, the raw material is upgraded by decreasing the iron content of the oxide. This is achieved by using carbon as reductant to convert some of the iron oxide in the ilmenite to metallic iron. The reactions occur in a molten slag within a temperature range of 1650-1750°C. (Geldenhuis and Pistorius 1999). The process yields two products: a titania-rich slag and molten iron. TiO_2 is used in the pigment industry, whereas the molten iron, after carburisation and desulphurisation, serves as a feed material for ductile iron castings. An electric furnace (AC or DC) provides the energy input (Bessinger et al. 1997). See figure 1:
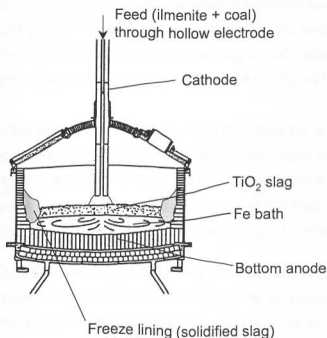

Figure 1: Schematic cross-section of a DC ilmenite smelter (after Stickler 1984)

In the continuous smelting of ilmenite ore, contact between the molten slag and furnace lining is prevented by the presence of solid slag banks. The latter are a requirement of the process, because there are no commercial refractories capable of withstanding the attack of the highly corrosive titania slags. The thickness of these banks is determined by a delicate equilibrium between the amount of energy delivered by the arc and the magnitude of the heat losses through the furnace walls. The temperature of the slag is independent of operation variables such as energy or power level. The only significant correlation involving the slag temperature is

that which indicates an increase in the value of this quantity with increasing TiO_2 (or decreasing FeO) in the slag.

The two main reactions that occur in the smelter are the following: (Grau and Poggi 1977)

Reduction of FeO from the slag:

$$FeO + C = Fe + CO \hfill [1]$$

Partial reduction of TiO_2 in the slag:

$$TiO_2 + 0.5C = TiO_{1.5} + 0.5CO \hfill [2]$$

Stable operation of the furnace requires a set relationship between ilmenite, energy and reductant inputs. Two inputs affect the furnace operation: the power input and the carbon feed rate (relative to the ilmenite feed rate). If the energy input is higher than that required by the given carbon input, the excess energy would superheat the slag above its liquidus temperature, which means that the slag can dissolve the freeze lining which protects the furnace wall.

If the energy input is lower than that required to balance the given carbon input, and if the available carbon reacts fully, the energy input would be insufficient to heat the slag to its liquidus temperature- thus the slag will be a mixture of liquid slag and precipitated solids. Such solids increase the apparent viscosity of the slag, with a resultant increase in the tendency for the slag to foam (this effect will be discussed at a later stage).

Grau and Poggi (1978) conducted studies on the physico-chemical properties of molten titania slags. In the smelting operation, a blend of ilmenite or and anthracite coal is fed continuously into electric furnaces equipped with in-line 24-in. graphite electrodes. The reduction process may be broadly described by the reactions:

$$Fe_2O_3 \quad C \rightarrow 2FeO \quad + CO$$
$$FeO + \ C \ \rightarrow \ Fe \quad + CO$$
$$2TiO_2 + C \rightarrow Ti_2O_3 + CO$$
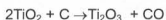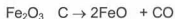
The thermodynamic feasibility of these reactions is illustrated by the free energy versus temperature plots in Figure 2:
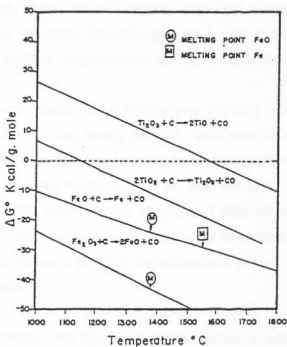
Figure 2: Free energy versus temperature plots for several reactions of interest to the smelting of ilmenite ores. (Grau and Poggi 1979)

The figure shows that the reduction of TiO_2 with carbon to produce Ti_2O_3 is favoured by an increase in temperature. The further reduction of Ti_2O_3 to TiO is seen to be more difficult and only minor proportions of this latter oxide should be expected to be present in the slag. When sufficient energy is made available to the process, the grade of the slag is directly controlled by the ratio of anthracite coal to ore in the feed. This ratio determines the FeO concentration in the slag and also the extent of Ti_2O_3 formation.

1.2 Overview of slag foaming

One of the major operational problems in the ilmenite smelter has been the foaming and consequent surges of molten slag. These foams or froths associated with the smelting practice are often so severe as to cause the shutdown of a furnace for a prolonged period of time. In the past foaming has been attributed to a sudden change in the slag's fluidity, due to temperature or compositional variations in the course of a smelting campaign. In the hope to solve this problem the physiochemical properties of the slags were studied on a laboratory scale. (Handfield and Charette 1971)

In the electric furnace smelting of the ilmenite ore, most of the iron oxide reduction probably occurs at the surface of the molten bath by reaction with the floating coal particles. The small droplets of liquid iron thus produced contain appreciable amounts of carbon and, during their

passage through the slag, some decarburization may take place. This reaction may also operate at the slag-metal interface. The CO gas produced in the above reaction bubbles through the slag and this explains the permanent boil observed in the furnace operation.

A condition sometimes encountered is the tendency of the slag to form a froth. Gas bubbles become enveloped in a film of slag which prevents their escape from the surface; the slag volume increases considerably and, in extreme cases, the operation must be interrupted to allow the foam to subside. The exact cause for this condition to appear is not known. Furthermore, it seems possible that there are a number of different situations which may cause a slag froth (MacPherson 1982). Among the properties of the molten slags which are believed to be related to the phenomenon of frothing, the viscosity is probably the one more frequently mentioned. (Grau and Poggi 1977)

In a possibly related observation, the high rates of gas injection in smelting reduction processes may in the presence of a sufficient quantity of slags, result in a substantial increase in the volume and interfacial area of the gas-in-slag dispersion, in a phenomenon known as slag foaming. (Ghag et al. 1998). The increase in the apparent slag volume resulting from the retention of gas bubbles within the slag phase can have a considerable impact on the efficiency of a smelting operation.

Whilst slag foaming has a significant impact on the efficiency of pyrometallurgical processes, there is little quantitative information relating the foaming ability of the slags to their properties. Laboratory scale slag foaming studies utilise one of two approaches: foaming by gas injection and foaming by gas bubbles evolved from chemical reactions. The former technique has dual advantages of control over gas flux and slag composition, but is limited to relatively larger bubbles. In contrast, in foams produced by gas evolved from chemical reactions, the gas evolution rate, bubble size distribution and slag composition are all functions of reaction time. The gas bubbles produced here, are significantly smaller. (Ghag et al, 1998).

Whereas slag foaming studies using gas injection show a linear relationship between gas residence times and slag viscosity, for foams produced by interfacial reactions the maximum foam height is inversely related to the slag viscosity. (Cooper and Kitchener 1959)

Experimental measurements (Ghag et al. 1998) show that the foaming ability of a solution can be expressed in terms of gas residence time. It has been shown that the gas residence time (time of retention of gas bubbles within the slag phase) increases with increasing solution viscosity and surface tension depression, and with decreasing bubble size.

Zhang and Fruehan (1995a, 1995b) investigated the effect of bubble size, carbonaceous particles, gas type and gas-phase pressure on slag foaming. Further research was conducted by Ozturk and Fruehan (1995) to study the effect of temperature on foaming. What follows below will be their findings and a brief discussion on each subject. Other factors affecting foaming such as viscosity and second phase particles will be discussed later. A schematic of the experimental apparatus for the electric probe technique is shown below.
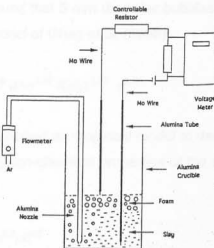

Figure 3: Schematic diagram illustrating the measurement of the foam index with the electric contact probes for foams generated by argon gas bubbling through the slag. (Zhang and Fruehan 1995a)

Slags without FeO were chosen to eliminate any reaction with the gas phase. The foam height was measured by the electric probe technique, and the foam heights at different flow rates were then compared with those obtained with argon gas injection. Argon injection generated more foam than helium and hydrogen. The large decreases in the foam index obtained with helium and hydrogen bubbling could be the result of the changes in the bubble size if the average bubble diameters were increased to 1.2 to 3 times that measured with argon. From these results it is seen that the foam stability of the liquid slag was affected by the type of gas used for bubbling. It can also be concluded that the foam index must also depend on the physical properties of the gas phase.

The density of the gas phase is an obvious factor. The amount of liquid in the foam supported by the gas bubble may depend on the momentum of the gas. Helium and hydrogen gases are

both lighter than argon, therefore, the gas velocities needed to generate the same amount of momentum for these gases are greater than that for argon.

Theoretically, it is expected that when different types of gas are used to generate bubbles in the liquid slag, the bubble diameter will depend on the gas density. According to the studies by the authors (Zhang and Freuhan 1995a), the foam index is inversely proportional to the average bubble diameter. Ghag *et al.* (1998) found that the gas residence times in foams generated from 5 mm diameter bubbles in calcium silicate slags at 1873K were suprisingly high, whereas Cooper and Kitchener (1959) found that 5 mm diameter bubbles did not produce foam in these slags. Equation [3] shows the model of Ghag *et al.* (1998):

$$\Sigma = 2.02 \times 10^6 \, \mu \Delta \sigma^{1.32} \, / (\rho g)^{2.32} \, d^{3.64} \qquad [3]$$

Zhang and Fruehan (1995b) developed an empirical model to describe the relationship between gas residence times and the physico-chemical properties of the slag phase for foams produced by gas injection.

$$\Sigma = 115 \mu^{1.2} / \sigma^{0.2} \rho d^{0.9} \qquad [4]$$

The model shows the gas residence time to be roughly proportional to the liquid viscosity and inversely related to the mean bubble size. It has been found that there is a poor correlation between the experimental data and the behaviour predicted by the high temperature model. The major sources of disagreements between the models are the sensitivity to the bubble diameter term and the surface tension of the liquid phase as described in the previous paragraph.

Clearly to be applicable to a range of systems, the model of foaming must take into direct consideration the mechanisms of foam stabilisation and their implications. (Ghag *et al.* 1998). A physical model of slag foaming was derived by using results of cold and hot model experiments (Ozturk & Fruehan, 1995). The governing factors of slag foaming have been clarified more in detail with this model. The effects of the physical properties of slag and metal on the foam height have been made clear.

It was confirmed that the bubble size evolved at the slag/metal interface is determined basically by the static balance between the buoyancy force and the adhesive force to the slag/metal interface, and the slag/metal interfacial tension and the surface tension of metals affect the foam height besides the surface tension and the viscosity of slag through the change in the

bubble size. This was confirmed by work done by Ogawa et al. (1993) and the experimental results are shown in table 1.

Table 1: Effects of physical properties on foaming behaviour (Ogawa et. al 1993)

	Foam height	Rupture rate of bubble film	Bubble Size	Void fraction of foam
Slag Viscosity	increase	decrease	No effect	decrease
Surface Tension	decrease	increase	increase	increase
Slag-Metal interfacial Tension	decrease	increase	increase	increase
Surface tension of metal	increase	decrease	decrease	decrease

1.2.1   The effect of Carbonaceous particles on slag foaming

Zhang and Fruehan (1995b) investigated the use of carbonaceous particles such as coke or coal char in controlling slag foaming. This is especially applicable in bath-smelting and other steel making processes. The foamability of the liquid slag in terms of the foam index has been determined with the presence of different amounts of coke and coal char particles. It was found that the foam index decreased significantly as the ratio of the total cross-sectional area of the particles to the liquid slag surface area increased. When the slag surface is covered with either coke or char particles the foam is totally suppressed regardless of the initial foam index.

To conclude: Coke and coal char have the same strong antifoam effect on the liquid slag. The foam index of the slag in the presence of carbonaceous particles depends on the coverage of the liquid slag surface by these particles. It was also found that the non-wetting particles such as coke and coal char ruptured the foam when they came into contact with the liquid slag bubble. It was concluded that two possible mechanisms of a carbonaceous particle rupturing a slag film are either the rapid thinning of the film driven by a difference between the instantaneous contact angle and equilibrium contact angle, or the "dewetting" of the liquid slag from the interface when the film is "bridged" by the particle.

1.2.2   Solid particles (apparent viscosity and foaming)

According to Pretorius *et al.* (1998) suspended second phase particles in the slag have a much greater impact on foaming than surface tension and slag viscosity. In lay terms, the slags that achieve the best foaming properties have a fluidity that falls between "creamy" and "fluffy", with "watery" and "crusty" on the extreme ends of the spectrum. This means that these second phase particles serve as gas nucleation sites, which lead to a high amount of favourable gas bubbles in the foaming slag. See Figure 4:
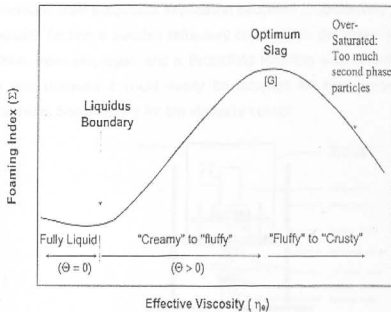

Figure 4:The relationship between the foaming index and the effective viscosity (Pretorius and Carlisle 1998)

The term effective viscosity was defined to relate the amount of second phase particles in the slag and viscosity as follows (Rosoe 1952):

$$\eta_\varepsilon = \eta(1\text{-}1.35\Theta)^{\text{-}2.5} \qquad [5]$$

η_ε	Effective viscosity of the slag
η	Viscosity of the molten slag
Θ	Volume fraction of precipitated solid phases

Figure 4 shows the relationship between the foaming index and the effective viscosity. As the relative effective viscosity is increased, the residence time of the gas bubbles in the slag is

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prolonged, extending the stability and subsequently the life of the foam. As seen in Figure 4, there is a maximum amount of second-phase particles that is beneficial for foam stability. Once this point is exceeded the slag becomes too "crusty"/oversaturated and the foaming index increases.

1.2.3 Effect of solid particles (apparent viscosity and foaming) on high titania slags

Handfield et.al (1971) conducted viscosity measurements as a function of temperature for high TiO_2 slags. Although numerous methods are available for the measurement of viscosity at room temperature, their successful application becomes progressively restricted as the temperature is increased. To find a suitable refractory container is the primary limitation. Molybdenum metal crucibles were employed and a Brookfield Rheolog was selected for its versatility, accuracy, price and because it could easily be adapted for high-temperature work under controlled atmosphere. See Figure 5 for the viscosity set-up:
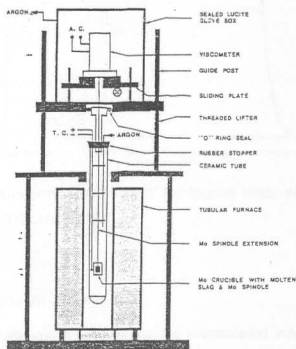

Figure 5:Schematic diagram of the viscosity setup. (Handfield and Charette 1971)

The results of the work for typical low- and high- TiO_2 slags are reproduced in Figure 6. The data in the figure show that titania slags are characterised by a low viscosity value (about 30 centipoise) when fully molten and that this value is not sensibly affected by the temperature of the molten slag. It may also be seen in the figure that the crystallization of the slag is accompanied by a rapid increase in viscosity.

The industrial significance of these measurements is as follows: Sorelslags (slag containing about 72% TiO_2) show that once these slags have melted completely they become very fluid. Their viscosity has been found to be of the order of 30 centipoises at all temperatures above their melting point, for a range of composition extending from 3 to 15 % FeO and from 80 to 67 % TiO_2. This slag has been known to build up a stable foam during smelting. It can thus be concluded that such a low viscosity in the molten region cannot be responsible for the stability of these froths. Other froth-stabilising factors are partial crystallisation and presence of Fe droplets. These low viscosity values are also an indication of the ease of convection within the melt and explain the speed with which titania slags have been known to corrode all refractory oxide containers.
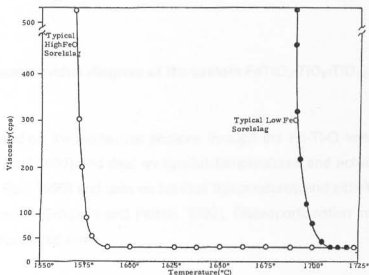

Figure 6: Viscosity versus temperature plots for typical high- and low-TiO_2 Sorelslags. (Handfield and Charette 1971)

1.3   Foaming in an Ilmenite Smelter

Slag composition and slag temperature cannot be manipulated independently in an ilmenite smelter. The furnace operates with a " freeze" lining of solidified slag against the furnace wall. The solidified slag serves to contain the molten slag, and is used because of the aggressive nature of the titania slag towards conventional refractories. Because the smelter operates with liquid slag in contact with solidified slag, and because the slag layer is expected to be well mixed, the slag temperature is expected to remain close to the liquidus temperature of the slag. Thus, changes in reductant and energy input are dependent on the slag liquidus. See Figure 7 for a conjectural liquidus diagram (Pistorius 2002).
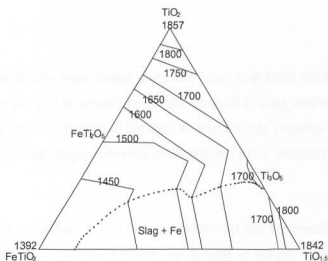
Figure 7 :Conjectural liquidus diagram of the system $FeTiO_3$-TiO_2-$TiO_{1.5}$ (Pistorius, 2002).

This diagram is based on the isothermal sections through the Fe-Ti-O ternary at 1500 °C and 1600 °C, (Eric and Pesl 1995) and data on liquidus temperatures and activities at 1500 °C and 1600 °C, (Eric and Pesl 1995) and data on liquidus temperatures and activities in the FeO-TiO_2 and TiO_2-$TiO_{1.5}$ binaries (Eriksson and Pelton, 1993). Disproportionation into metallic iron and slag occurs below the dotted line.

Two approaches may be followed regarding conditions which give rise to foaming. It can be reasoned that the furnace temperature and the slag composition influence foaming. If the furnace temperature goes above the liquidus temperature of the slag, the slag viscosity is lowered and the chances of foaming are reduced. If Ti^{4+} is reduced to Ti^{3+} the slag liquidus is also lowered due to the formation of Ti_2O_3 and the same argument is applied as the above. On the other hand it can be reasoned that lower FeO levels gives a higher melting point, thus the slag temperature is lower than the liquidus which can induce more foaming. Thus the slag foaming is directly related to the slag composition.

1.4   Conclusion

It can be concluded that: firstly, high titania slags are very fluid once completely molten and any degree of superheating will not improve the fluidity of such a slag, secondly, the reported poor fluidity of high titania slags is most probably due to incomplete melting, thirdly, FeO acts as a very potent flux in high titania slags, lowering their melting point sensibly, without affecting their viscosity.

As discussed previously in section 1.3, it can be seen that the temperature of the furnace and the melting point of the slag, will determine the extent to which foaming occurs. Viscosity measurements have shown that more viscous slags are more prone to foam (Handfield et al, 1971). In the smelter this can be overcome by increasing the furnace temperature. The foams produced during ilmenite smelting can be attributed to CO generation during the reduction of FeO. Thus, adding more coal to the smelter would only aggravate foaming. This is not in accordance to bath-smelting and other steel making processes where coke and char have a strong antifoam effect (Zhang and Fruehan, 1995b).