

# Partial slag solidification within an ilmenite smelter

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## Abstract

Within ilmenite smelters, the slag is at a temperature just above its liquidus (because the furnace operates with a slag freeze lining), and the metal bath is at a temperature which is approximately 150°C lower than the slag temperature. As a result, solidification of the slag in contact with the metal is expected, and was indeed detected with sounding bars in operating furnaces. Samples of the solidified layer were obtained from a DC ilmenite smelter which had cooled with its contents intact. Analysis showed parts of the layer to be close to anosovite ( $\text{Ti}_3\text{O}_5$ ) in composition; in all cases, the solid contained much less FeO than the primary pseudobrookite which forms during bulk slag solidification after tapping. Equilibrium calculations show that these compositions can result from reaction of initially FeO-rich pseudobrookite with dissolved carbon in the metal bath. The presence of this layer of near-anosovite material in the furnace has possible implications for settling of metal and for the furnace energy balance; the latter was explored with thermodynamic calculations.

## Introduction

This paper deals with the identity of a solid layer which forms between the layers of liquid slag and liquid metal in an ilmenite smelter. It is proposed that the layer can achieve a composition close to that of anosovite ( $\text{Ti}_3\text{O}_5$ ) through reaction of the slag with dissolved carbon in the metal, at the slag-metal interface. The possibility of this reaction is tested by thermodynamic calculations, and the compositions of interlayer samples obtained from a furnace excavation are presented.

In an ilmenite smelter, there is a large temperature difference – typically about 150°C – between the molten iron and the molten slag within the furnace.<sup>1</sup> The slag is at a temperature which is only slightly higher than its liquidus temperature (because of the use of a freeze lining on the furnace walls), whereas the underlying metal bath is colder. It was proposed that this temperature difference plays an important role in the mechanism that maintains the slag bath composition close to  $\text{M}_3\text{O}_5$  stoichiometry.<sup>1</sup> In this paper, we examine the possibility that partial solidification at the interface, followed by further reduction of FeO from the slag (by dissolved carbon in the metal), can lead to substantial enrichment of the solidified slag at the interface, such that the composition of the solid approaches  $\text{Ti}_3\text{O}_5$ . This proposed reaction sequence builds on the calculated significant departure from chemical equilibrium in ilmenite smelting.<sup>2</sup> The departure from chemical equilibrium is such that the partial pressure of oxygen for equilibrium between  $\text{TiO}_2$  and  $\text{Ti}_2\text{O}_3$  in the slag is higher than for the Fe(metal)/FeO(slag) couple, which in turn gives a much higher oxygen activity than the C(metal)/CO(gas) couple.<sup>3</sup> While it has been argued that the calculated difference in the oxygen activity for the  $\text{TiO}_2/\text{Ti}_2\text{O}_3$  and Fe/FeO couples is an artifact of the slag model used in the FactSage calculations,<sup>4</sup> there is little doubt that the difference with the C/CO couple is large, as confirmed by oxygen probe measurements.<sup>5</sup> Some calculated values are presented later in the paper; as an indication of the size of the effect, it can be noted that the typical carbon content of the iron product in ilmenite smelting is 2%,

whereas the carbon content for equilibrium with the molten slag would be one order of magnitude smaller than this, around 0.2%. This means that carbon in the metal can reduce  $\text{TiO}_2$  and  $\text{FeO}$  in the slag, at the slag-metal interface.

It is hence proposed that slag close to the slag-metal interface undergoes both a physical change (partial solidification because of the lower temperature) and a chemical change (further reduction of  $\text{TiO}_2$  to  $\text{Ti}_2\text{O}_3$ , and  $\text{FeO}$  to  $\text{Fe}$ ). Both the decrease in temperature and further slag reduction will lead to increased solidification of the slag close to the interface with the metal bath (because the melting point of the slag increases as the  $\text{FeO}$  content decreases<sup>1</sup>). Operators of direct-current (DC) furnaces do report the presence of a solid layer at the slag-metal interface; this layer is detected as a barrier to the vertical descent of sounding bars which are inserted through ports in the furnace roof, and the layer has also been visually observed above the metal layer, when looking into the metal tap hole. Our analysis of initial samples obtained from the Exxaro KZN Sands ilmenite smelter (located in Empangeni, South Africa) showed the interlayer to be close to  $\text{Ti}_3\text{O}_5$  in composition; plant personnel also reported that previous analysis of similar samples had found the interlayer to contain titanium oxycarbide. During excavation of the Exxaro KZN Sands Furnace 2 after a water ingress incident in February 2008<sup>6</sup> samples which could be positively identified as originating from the slag-metal interface were collected; the analyses of these samples are reported in this paper.

## **Examination of furnace samples**

### **Sampling**

Samples from five locations were selected for analysis by X-ray diffraction and electron microprobe. All of the samples were from the lowest part of the slag layer, close to the metal. Within this plane, the samples were taken from close to the furnace wall, at the following positions: northwest, northeast, north (above the metal taphole) and south (below the slag taphole). Samples were also taken from the centre of the furnace, beneath the electrode. Sample preparation was particularly challenging because the intergrown metal and oxide in the samples did not permit cutting with a diamond saw; a ceramic saw was used instead.

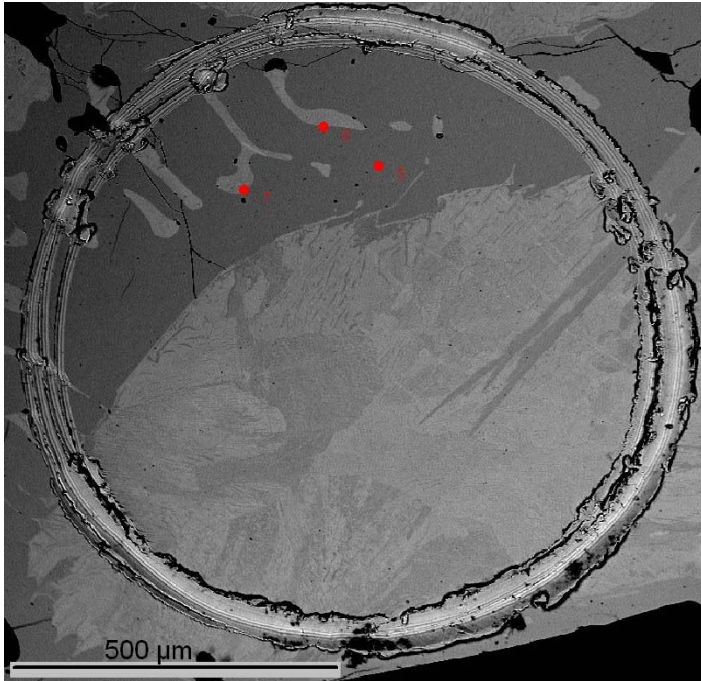
### **Microstructure**

A typical backscattered electron image of the metal-oxide association in these samples can be seen in Figure 1. The metal clearly consists of two phases, the darker phase being cementite. The relatively large size of the crystallites points to a lengthy cooling period in the furnace. Oxide and metal compositions were measured close to their interfaces.

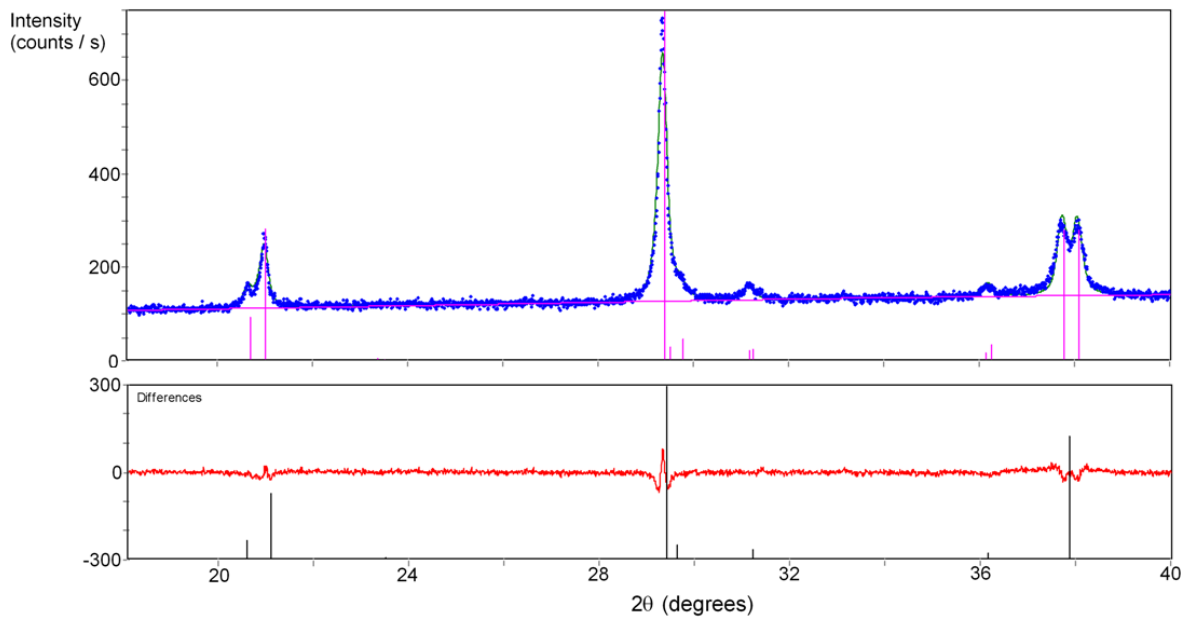
### **X-ray diffraction**

Samples without macroscopic metal particles were crushed and milled in a micronising mill for powder XRD measurement in a PANalytical X'pert Pro powder diffractometer. The measured powder patterns were then quantified with the Rietveld program Autoquan<sup>7</sup>.

The samples contained one of two  $\text{M}_3\text{O}_5$  phases: the conventional "karrooite" orthorhombic  $\text{M}_3\text{O}_5$  phase and the monoclinic anosovite phase (nearly pure  $\text{Ti}_3\text{O}_5$ ). The monoclinic phase has a characteristic peak splitting at  $38^\circ 2\theta$  (using  $\text{Co K}_\alpha$  radiation), whereas the orthorhombic phase shows a single peak; see Figure 2. Anosovite was found only in the samples taken from the northwest and northeast positions in the furnace; all other samples contained orthorhombic  $\text{M}_3\text{O}_5$ . The proportion of  $\text{M}_3\text{O}_5$  in all samples varied from 87% to 100%, with the rest being ferrite and cementite.



**Figure 1.** Backscattered electron image of the interface between oxide slag (dark phase in the upper part of the marker circle) and metal. The metal consists of intergrown ferrite (brighter) and cementite (darker). Sample 2814 (NW)



**Figure 2.** Diffraction pattern of monoclinic (anosovite) phase (upper graph), with Rietveld analysis, and difference between fitted and measured pattern (lower curve). The vertical lines on the diffraction pattern show the peak positions of the monoclinic phase, whereas the lines on the (lower) difference pattern show the peak positions of the orthorhombic phase. Note the characteristic splitting of the peak at  $38^\circ$   $2\theta$  for the monoclinic phase.

## Compositional variation of phases

### Oxide phase

The compositions of the phases were determined with a Cameca SX100 electron microprobe at the University of Pretoria (20kV accelerating voltage; 20nA probe current). The concentrations of all elements (including oxygen, but excluding carbon for the metal phases) were measured. The distribution of titanium between trivalent and tetravalent oxidation states was calculated by assuming that the phase followed  $M_3O_5$  stoichiometry, with all Fe, Mg and Mn divalent, and Cr,

Al and V trivalent. The calculated compositions are given in Table 1. The compositions show extreme depletion in iron compared with bulk slag. In addition, samples from the NW and NE positions generally have the highest  $Ti^{3+}$  contents, and XRD samples from these positions had the anosovite structure. The observation that the extent of FeO reduction from the slag is smaller beneath the electrode ("Central" position) is consistent with the strong arc stirring, which would tend to prevent slag solidification at the interface. It appears that, as this furnace cooled after the water ingress incident, different extents of reaction between solidified slag and dissolved carbon were preserved at the different locations within the slag, at the slag-metal interface.

**Table 1:** Composition of  $M_3O_5$  oxide phase in slag samples taken from close to the slag-metal interface, as measured by microprobe. Compositions are given as molar amounts of cations in the  $M_3O_5$  phase, except for the calculated FeO and  $Ti_3O_5$  contents, which are mass percentages. "Position" gives the original sample location in the furnace, and "Phase" the identity of the  $M_3O_5$  phase in samples from the same position subject to X-ray diffraction; "M" is monoclinic (anosovite) and "O" is orthorhombic (karrooite). Averages and standard deviations are given for all the phases analysed. A typical  $M_3O_5$  composition from bulk slag is shown for comparison.

Position	Sample	Phase	Fe	Mn	Ti <sup>4+</sup>	Ti <sup>3+</sup>	Mg	Al	V	Cr	%FeO	%Ti <sub>3</sub> O <sub>5</sub>
NW	2814_1	M	0.01	0.00	1.09	1.72	0.09	0.08	0.02	0.00	0.20	87.3
NW	2814_2	M	0.01	0.00	1.09	1.73	0.08	0.08	0.02	0.00	0.22	87.6
NE	3639_23	M	0.01	0.01	1.14	1.62	0.12	0.09	0.02	0.00	0.17	82.8
NE	3941_28	M	0.01	0.01	1.13	1.63	0.12	0.09	0.02	0.00	0.26	83.2
NE	3941_38	M	0.11	0.06	1.24	1.43	0.07	0.05	0.03	0.01	3.56	72.1
NE	3941_39	M	0.11	0.06	1.24	1.43	0.07	0.05	0.03	0.01	3.52	72.0
N	4217_33	O	0.07	0.05	1.20	1.52	0.07	0.05	0.03	0.01	2.39	76.4
N	4217_34	O	0.07	0.05	1.20	1.52	0.07	0.05	0.03	0.01	2.37	76.5
S	2957_1	O	0.09	0.06	1.26	1.39	0.11	0.05	0.03	0.01	2.92	70.3
S	2957_2	O	0.10	0.06	1.27	1.37	0.11	0.05	0.03	0.01	3.20	69.4
S	2957_3	O	0.09	0.06	1.27	1.39	0.12	0.05	0.02	0.00	3.00	70.1
S	3208_8	O	0.10	0.05	1.26	1.39	0.11	0.05	0.03	0.00	3.31	70.2
S	3208_9	O	0.10	0.05	1.26	1.38	0.11	0.05	0.03	0.00	3.32	70.0
S	3208_10	O	0.10	0.05	1.26	1.40	0.11	0.05	0.03	0.00	3.30	70.7
Central	3327_1	O	0.20	0.04	1.31	1.30	0.07	0.05	0.03	0.01	6.39	65.4
Central	3327_2	O	0.19	0.04	1.30	1.31	0.07	0.05	0.03	0.01	6.24	65.6
Central	3408_1	O	0.20	0.05	1.31	1.30	0.06	0.05	0.03	0.01	6.32	65.2
Central	3408_2	O	0.20	0.05	1.31	1.30	0.06	0.05	0.03	0.01	6.32	65.0
Central	3510_1	O	0.20	0.04	1.31	1.29	0.07	0.05	0.03	0.01	6.44	64.7
Central	3510_2	O	0.20	0.04	1.31	1.30	0.07	0.05	0.03	0.01	6.39	65.2
All	Av		0.11	0.04	1.24	1.44	0.09	0.06	0.03	0.01	3.49	72.5
	SD		0.07	0.02	0.07	0.14	0.02	0.01	0.01	0.00	2.24	7.4
Bulk slag			0.38	0.06	1.49	0.95	0.05	0.05	0.01	0.005	12.2	47.4

## Metal

The analytical data for the metal phases, ferrite and cementite, are given in Table 2. Carbon was not analysed for, and therefore the analyses for cementite will only add up to a total approaching 93.3% (the Fe content of  $Fe_3C$ ). Noteworthy are the low Ti content in both the metal phases as well as the slightly higher Cr contents in cementite. The overall carbon content in the metal phases was estimated, by determining the relative amounts of ferrite and cementite by image analysis. Based on a limited number of images (7) the carbon content was estimated as 3.7% with a standard deviation of 0.7%; little different from the typical bulk metal composition.

**Table 2:** Compositions of metallic phases (mass percentages)

Phase	Position	Ti	V	Cr	Mn	Fe	Nb	Total
Cementite	NW	0	0.11	0.09	0.03	93.38	0.04	93.66
	NW	0.01	0.02	0.05	0.03	93.93	0	94.05
	NW	0.02	0.07	0.13	0.02	93.14	0.07	93.44
	NE	0.01	0.05	0.08	0.02	93.64	0	93.79
	NE	0.01	0.19	0.18	0.02	92.75	0	93.14
	NE	0	0.17	0.17	0.01	93.21	0.04	93.59
Ferrite	NW	0.02	0.01	0.03	0	100.13	0.04	100.24
	NE	0.01	0.02	0	0.02	99.33	0.02	99.4
	NE	0.03	0	0	0	99.88	0.04	99.95
	N	0.04	0.01	0.02	0	99.33	0	99.4
	S	0.09	0.01	0	0	99.33	0	99.43
	S	0.03	0	0.03	0	99.63	0	99.7
	S	0	0	0.01	0.02	100.32	0.03	100.38
	Central	0.01	0	0.03	0	100.28	0	100.33

## Calculations: formation and effect of interlayer

### Assumed conditions

The slag composition was taken to be 54.0% TiO<sub>2</sub>, 28.8% Ti<sub>2</sub>O<sub>3</sub>, 12.1% FeO, 1.8% MnO, 1.1% Al<sub>2</sub>O<sub>3</sub>, 1.0% SiO<sub>2</sub>, 0.9% MgO, 0.16% Cr<sub>2</sub>O<sub>3</sub>, 0.082% CaO and 0.015% K<sub>2</sub>O, which is typical (this is also the basis of the "bulk slag" pseudobrookite composition in Table 1). The calculated solidification behaviour of slag of this composition is given elsewhere.<sup>8</sup> Equilibrium predictions were made with FactSage 6.0,<sup>9</sup> using the solution phase models in the FToxid database (for oxides, such as the liquid slag and pseudobrookite solid), and the liquid metal model from the FSstel database. The metal phase was assumed to be 98% Fe and 2% C, with additional dissolution of a small amount of titanium in some cases. Where reactions involved the gas phase, this was assumed to be pure CO at 1 atm. Two temperatures were considered: 1650°C (assumed slag temperature), and 1500°C (assumed metal temperature). For these conditions, the activities of the main slag and metal species are given in Table 3, and the oxygen activity for equilibrium with the three couples, Fe/FeO, TiO<sub>2</sub>/Ti<sub>2</sub>O<sub>3</sub> and C/CO, in Table 4. Standard free energy values, for the calculation of equilibrium constants, were taken from FactSage.

**Table 3.** Activities in metal and slag phases (as used for equilibrium calculations) at 1773K and 1923K.

Species	Activity		Reference state
	1773K	1923K	
TiO <sub>2</sub>	0.62	0.61	pure liquid
TiO <sub>1.5</sub>	0.21	0.22	pure liquid
FeO	0.041	0.044	pure liquid
Fe	0.88	0.88	pure liquid
C	0.14	0.12	graphite

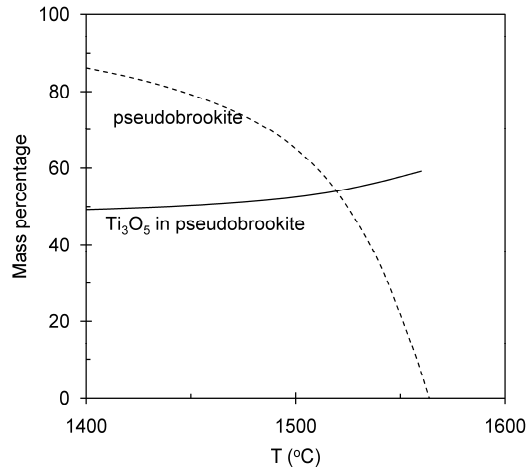
**Table 4.** Partial oxygen pressure (in atm) for equilibrium with the different couples

Reaction	1773K	1923K
2FeO = 2Fe + O <sub>2</sub>	2.0×10 <sup>-12</sup>	3.1×10 <sup>-11</sup>
2CO = 2C + O <sub>2</sub>	9.8×10 <sup>-15</sup>	4.5×10 <sup>-14</sup>
4TiO <sub>2</sub> = 4TiO <sub>1.5</sub> + O <sub>2</sub>	3.0×10 <sup>-11</sup>	1.7×10 <sup>-9</sup>

### Solidification behaviour

Some detail of the predicted solidification behaviour is given in Figure 3, which shows that formation of pseudobrookite (the dominant solid solution phase, with M<sub>3</sub>O<sub>5</sub> stoichiometry) is

predicted to start below the liquidus temperature of 1564°C, with a rapid increase in the amount of pseudobrookite with decreasing temperature (the balance of the phase composition is largely liquid slag, and a small fraction of rutile below 1540°C). The proportion of Ti<sub>3</sub>O<sub>5</sub> in the pseudobrookite is also shown in the graph; this was calculated by assuming the pseudobrookite to be a mixture of FeTi<sub>2</sub>O<sub>5</sub>, Ti<sub>3</sub>O<sub>5</sub>, MnTi<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>TiO<sub>5</sub>, MgTi<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>TiO<sub>5</sub>. As Figure 3 shows, the proportion of Ti<sub>3</sub>O<sub>5</sub> is higher in the first (higher-melting) pseudobrookite that forms, but the proportion of Ti<sub>3</sub>O<sub>5</sub> remains below 60% throughout solidification, much less than the nearly pure Ti<sub>3</sub>O<sub>5</sub> found by microanalysis, for the samples from the northwest and northeast positions.



**Figure 3.** Predicted solidification behaviour of the slag with composition 54.0% TiO<sub>2</sub>, 28.8% Ti<sub>2</sub>O<sub>3</sub>, 12.1% FeO, 1.8% MnO, 1.1% Al<sub>2</sub>O<sub>3</sub>, 1.0% SiO<sub>2</sub>, 0.9% MgO, 0.16% Cr<sub>2</sub>O<sub>3</sub>, 0.082% CaO and 0.015% K<sub>2</sub>O. The broken line gives the proportion of pseudobrookite in the mixture (the balance is mostly liquid, and below 1540°C about 5% rutile); the solid line shows the proportion of the pseudobrookite which is Ti<sub>3</sub>O<sub>5</sub>.

### Possibility of oxycarbide formation

Titanium(II)oxide (TiO) and titanium carbide (TiC) form a continuous solid solution.<sup>10</sup> Data on activities in the solid solution are rather limited, but recent calculations (Gibbs-Duhem integration) by Kwon and Kang,<sup>11</sup> based on the experimental data of Ouensanga,<sup>12</sup> showed the departure from ideal behaviour to be small. The possibility of forming the oxycarbide solid solution was evaluated by considering the following two reactions:



The oxygen activities which were considered spanned the range of the values listed in Table 4; the results are presented in Figure 4, as the sum of the equilibrium activities of TiO and TiC. The principle is that, if the sum of the activities equals 1, then an ideal solid solution of TiO and TiC can form by reactions (1a) and (1b) as a separate phase; if the sum of the activities is smaller than 1, then titanium oxycarbide cannot form. The results show that the latter is the case: titanium oxycarbide cannot form under the conditions prevailing at the slag-metal interface. (It is worth noting that, if the slag were to come into contact with pure graphite or carbon-saturated iron, the resulting higher carbon activity and lower oxygen activity would allow oxycarbide formation, but because in reality the carbon activity of iron with 2% C is much lower, the oxycarbide cannot form.) Also, there was no evidence at all, from X-ray diffraction or the microstructures of the samples, of oxycarbide formation.

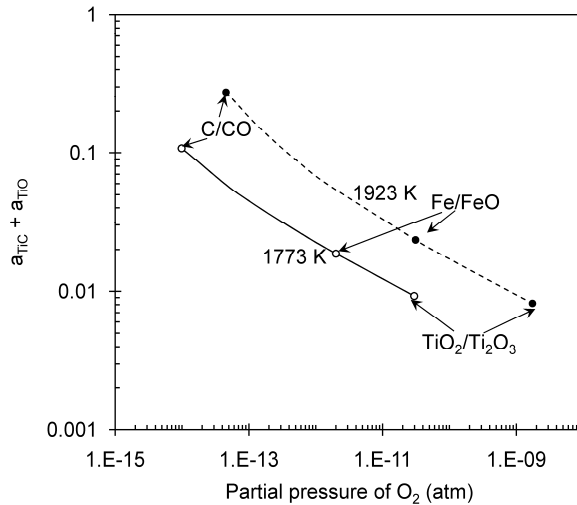
A further indication that titanium oxycarbide does not form at the slag-metal interlayer is given by the relationship between the titanium and carbon contents of the metal. Plant data show the titanium content of the metal to be low, and correlated with the carbon content of the metal by the following relationship (for mass percentages of titanium and carbon):

$$[\% \text{Ti}] = 0.008 [\% \text{C}]^{2.54} \quad (2)$$

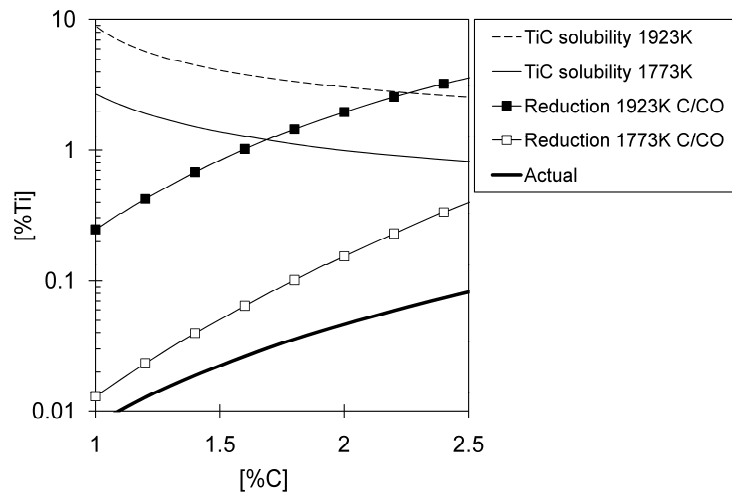
If titanium carbide were equilibrated with the metal, one would expect an inverse relationship between the titanium and carbon contents, according to the reaction



where the pointed brackets indicate a solid, and the square brackets species dissolved in the metal; if this equilibrium held titanium and carbon would be inversely related by  $K = a_{\text{TiC}} / a_{\text{Ti}} a_{\text{C}}$ . Figure 5 compares the predicted titanium content of the metal for equilibrium according to equation (3) with the actual titanium content; the actual titanium content is much lower than for TiC saturation (and does not follow an inverse relationship).



**Figure 4.** Calculated sum of the equilibrium activities of solid TiC and TiO, for slag in contact with Fe containing 2%C, at 1773K and 1923K, for different oxygen activities. The calculated partial oxygen pressures for the three different couples are arrowed. The low equilibrium activities of TiO and TiC indicate that the Ti(O,C) solid solution cannot form at the slag-metal interface.



**Figure 5.** Comparison of the actual relationship between the titanium and carbon contents of the metal, with the predicted equilibrium relationship for TiC saturation, and for reduction of the TiO<sub>2</sub> from the slag by dissolved carbon in the metal. The actual titanium content of the metal is much less than for TiC saturation, indicating that TiC is not present at the metal-slag interface.

The actual titanium content is similar to that calculated for the following reduction equilibrium:

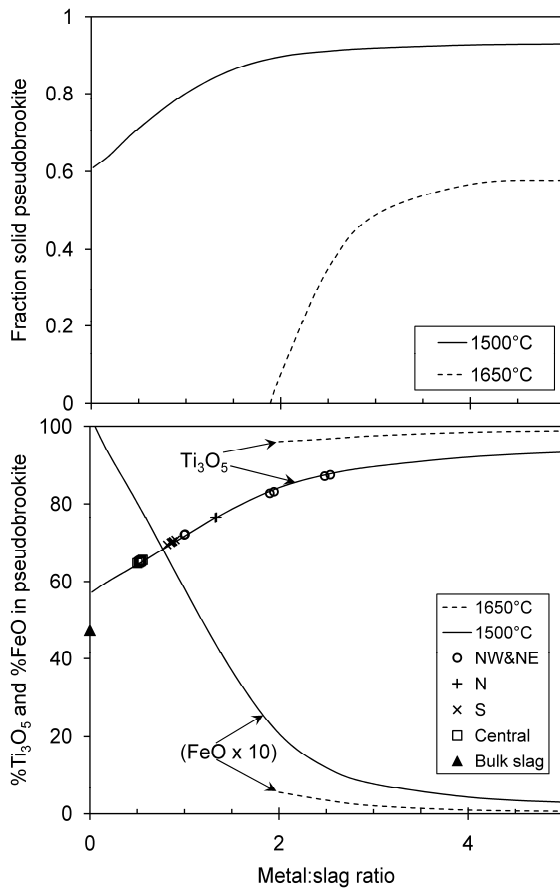


For prediction of the equilibrium titanium and carbon contents according to reaction (4), the activity data of Ozturk and Fruehan<sup>13</sup> were used. Figure 5 shows that the titanium-carbon relationship for equilibrium of reaction (4) at 1773 K is similar to the actual relationship.

Both considerations – possible reduction of the slag to TiC and TiO, and the Ti-C relationship in the metal – indicate that titanium oxycarbide is not expected to form at the slag-metal interface.

## Ti<sub>3</sub>O<sub>5</sub> formation

The possibility that the slag-metal interlayer can approach Ti<sub>3</sub>O<sub>5</sub> in composition – by reaction of the partially solidified slag with carbon in the metal – was evaluated by considering the equilibrium composition for reaction of slag (with the composition as stated earlier) with metal (Fe-2%C), in various ratios. This was chosen to approximate the condition in the furnace, where the observation of a fixed layer at the slag-metal interface implies that the slag is partially or fully solidified, immobile, and hence trapped in contact with the metal bath. The results, for the two temperatures of 1773 K and 1923 K, are presented in Figure 6. (Note that – as Figure 3 shows – at 1773 K the slag is more than half solidified before any reaction with the metal bath, but the solid pseudobrookite is far from Ti<sub>3</sub>O<sub>5</sub> in composition.)



**Figure 6.** Equilibrium slag composition, for reaction of the slag with Fe-2%C in various mass ratios. The upper figure shows the proportion of the slag which is solid pseudobrookite following reaction, and the lower figure the proportion of the pseudobrookite which is Ti<sub>3</sub>O<sub>5</sub>, and the FeO content of the pseudobrookite (the latter multiplied by 10 for better visibility). Data points in the lower figure show the actual measured Ti<sub>3</sub>O<sub>5</sub> contents of pseudobrookite (from Table 1) for the different positions along the slag-metal interface, and for bulk slag; these are arbitrarily plotted along the 1500°C curve.

Figure 6 illustrates that it is feasible for the interlayer to approach Ti<sub>3</sub>O<sub>5</sub> in composition, by carbon in the metal nearly fully reducing FeO from the slag, and partially reducing the TiO<sub>2</sub> to Ti<sub>2</sub>O<sub>3</sub>. At 1773 K, the FeO content of the pseudobrookite is below 2%, and the slag composition hence approaches pure Ti<sub>3</sub>O<sub>5</sub>, even at a metal:slag mass ratio as low as 2. For a reaction temperature of 1923 K, the FeO content of the solid M<sub>3</sub>O<sub>5</sub> phase is even lower. In comparison, the mass percentage of Ti<sub>3</sub>O<sub>5</sub> in the furnace samples (Table 1) range from around 65% for the Central samples, to 83-88% for the northwest and northeast samples.

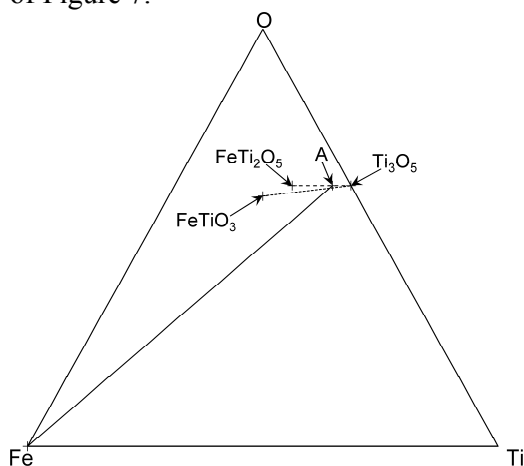
## Effect of Ti<sub>3</sub>O<sub>5</sub> interlayer formation on energy balance

The actual extent of the solid interlayer in operating furnaces is not known, but observations of sounding bar movement indicate the interlayer to extend over much of the furnace diameter, and to be sufficiently thick to resist penetration by sounding bars. The presence of a significant mass



of solid  $\text{Ti}_3\text{O}_5$  in the furnace, together with metal and liquid slag, can have implications for the furnace energy balance. Because the furnace operates with a freeze lining, close regulation of the energy balance is essential, and hence it is important to assess whether this interlayer may affect the furnace energy balance. The possible effect that is considered here is where a  $\text{Ti}_3\text{O}_5$  interlayer has formed, and subsequently reacts with ilmenite feed. The  $\text{Ti}_3\text{O}_5$  can react chemically with ilmenite, with the trivalent titanium in the  $\text{Ti}_3\text{O}_5$  acting as a reductant, to yield titanium slag and metallic iron as products.

For an initial assessment of the effect of such reaction of  $\text{Ti}_3\text{O}_5$ , the simplified ternary Fe-Ti-O system was considered, taking the ilmenite feed to be  $\text{FeTiO}_3$ , and assuming the slag product to follow  $\text{M}_3\text{O}_5$  stoichiometry, with 10% FeO (by mass) in the slag. The slag product (and CO, for the case of reduction by C for comparison) were assumed to be at  $1650^\circ\text{C}$ , with the ilmenite feed at  $25^\circ\text{C}$ , and the  $\text{Ti}_3\text{O}_5$  interlayer at  $1500^\circ\text{C}$ . The reaction path is shown in the ternary diagram of Figure 7.



**Figure 7.** Ternary diagram (compositions as mole fractions) showing the reaction path if  $\text{Ti}_3\text{O}_5$  (solid interlayer) reacts with ilmenite feed ( $\text{FeTiO}_3$ ) to form  $\text{M}_3\text{O}_5$  slag containing 10% FeO by mass (point A) and a small amount of Fe; the resulting overall composition is at the intersection of the A-Fe and  $\text{FeTiO}_3$ - $\text{Ti}_3\text{O}_5$  joins.

As Figure 7 indicates, reaching 10% FeO in the slag involves reaction of  $\text{Ti}_3\text{O}_5$  with a smaller amount of  $\text{FeTiO}_3$  (the mass ratio is 2.9:1); the amount of Fe metal formed is small (74 kg per tonne of ilmenite). Table 5 compares the enthalpy effects of this reaction path with that of reduction with carbon. This shows that reaction of ilmenite with a  $\text{Ti}_3\text{O}_5$  requires more energy – per tonne of ilmenite – than does reduction with carbon; the main reason is the heat required to melt the large volume of  $\text{Ti}_3\text{O}_5$  that mixes and reacts with the ilmenite to form the slag. In addition, if the  $\text{Ti}_3\text{O}_5$  reacts with the ilmenite feed, the carbon that was fed with the ilmenite remains unreacted. Heating of the unreacted carbon to the slag temperature also requires energy, amounting to 70 kWh per tonne of ilmenite (for the case considered here, where 89 kg of carbon would react per tonne of ilmenite). The overall effect is that reaction of the  $\text{Ti}_3\text{O}_5$  with ilmenite feed consumes more energy, by approximately 200 kWh per tonne of ilmenite, than does reaction with carbon. This is significant compared with the typical energy requirement of approximately 1000 kWh per tonne of ilmenite. The implication is that, if  $\text{Ti}_3\text{O}_5$  has formed and later starts reacting, the furnace would experience an energy deficit, which may lead to foaming due to incomplete melting of slag.

## Conclusion

The solidified slag layer immediately above the metal layer in a DC ilmenite smelter furnace is significantly lower in iron oxide than the bulk slag, and approaches  $\text{Ti}_3\text{O}_5$  in some cases; the metal composition is similar to bulk metal. The change in slag composition has been shown to be consistent with predicted equilibrium conditions at this interface; the dissolved carbon in the

metal can further reduce FeO from the solid slag, without forming titanium oxycarbide. This solid near-Ti<sub>3</sub>O<sub>5</sub> layer would cause an energy deficit should it start reacting with ilmenite feed.

**Table 5.** Calculated effect on the energy balance of Ti<sub>3</sub>O<sub>5</sub> reacting with ilmenite feed, instead of the ilmenite reacting with carbon; all numbers are in kWh per tonne of ilmenite feed.

Situation	Energy for reaction	Energy to heat excess C	Total
Reference case: reduction with C	978	0	978
Ilmenite reduced by Ti <sub>3</sub> O <sub>5</sub>	1120	70	1190

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