Process mechanisms in ilmenite smelting

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Synopsis

It has previously been observed that industrial high-titania slags display a compositional invariance, remaining close to stoichiometric M_3O_5. The present study focuses on this invariance and the phenomena which may cause it. The invariance was studied using thermochemical calculations and a mechanism is proposed for the observed behaviour. The mechanism suggests that a combination of thermochemical equilibrium and transient slag solidification and melting results in the observed compositional invariance. The proposed mechanism provides new insights and prompts questions about other mechanisms in the smelting process.

INTRODUCTION

Industrial high-titania slags, produced by ilmenite smelting, display a compositional invariance close to the stoichiometric M_3O_5 composition[1]—that is, the chemical compositions of the slags are such that the solidified slag largely consists of a single phase which contains five oxygen anions for every three metal cations. The smelting process has previously been studied to determine the cause of this invariance[2-5], but the mechanism remains uncertain. It has been suggested that the eutectic groove present on the phase diagram of the TiO_2-$FeTiO_3$-Ti_2O_3 system and phase chemistry effects may serve to constrain the slag to a composition close to the M_3O_5[3]. Reaction equilibrium and kinetic effects have also been mentioned as possible causes[2]. However, arguments against all of these phenomena as possible explanations of the observed behaviour have also been presented[2,5].

The compositional invariance—which implies that the concentrations of divalent and trivalent cations (mainly Fe^{2+} and Ti^{3+}) are related—has several practical implications. For example, some chlorine-route producers of TiO_2 pigment specify a maximum Ti_2O_3 content in the high-titanium slag feedstocks. In the work presented here, a simplified slag system consisting of only FeO, TiO_2 and Ti_2O_3 was considered. The work described in this paper is part of a Ph.D. study at the University of Pretoria[6].

Thermochemical characteristics of the system

Before focusing on the compositional invariance, it is necessary to provide some background on the thermochemical characteristics of the simplified high-titania slag system used during this study. All the diagrams presented here are based on results from the thermodynamic software package FactSage 5.2[7]. Figure 1 contains liquidus diagrams of the system. For these diagrams Magnéli phases were omitted from the calculations, because these phases have not been detected in high-titania slags[3]. In addition to liquidus isotherms, the eutectic groove, the M_3O_5 composition and the slag/(slag + Fe°) phase boundary are shown on the liquidus diagrams.

Figure 2 shows a constant-FeO section through the TiO_2-FeO-Ti_2O_3 ternary diagram (at 15% FeO by mass). The intersections with the eutectic groove (at 56.6% TiO_2 and 1582.4°C) and stoichiometric M_3O_5 composition (at 51.8% TiO_2 and 1590.2°C) are again visible.

Finally, Figure 3 shows the composition trajectories of the remaining liquid during solidification. Evidently the composition of liquid slag with a starting composition above the M_3O_5 join (that is, richer in TiO_2 and poorer in FeO and Ti_2O_3 than stoichiometric M_3O_5) is modified through solidification towards and into the eutectic groove. The composition of liquid slag with an initial composition below the M_3O_5 join is modified towards the slag/(slag + Fe°) phase boundary.

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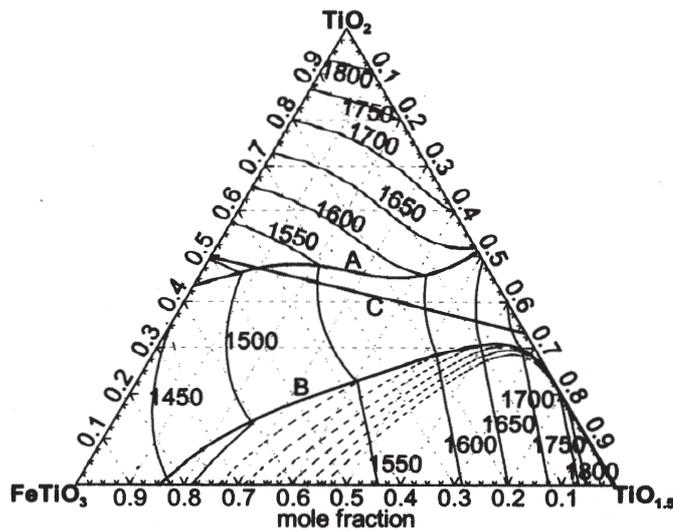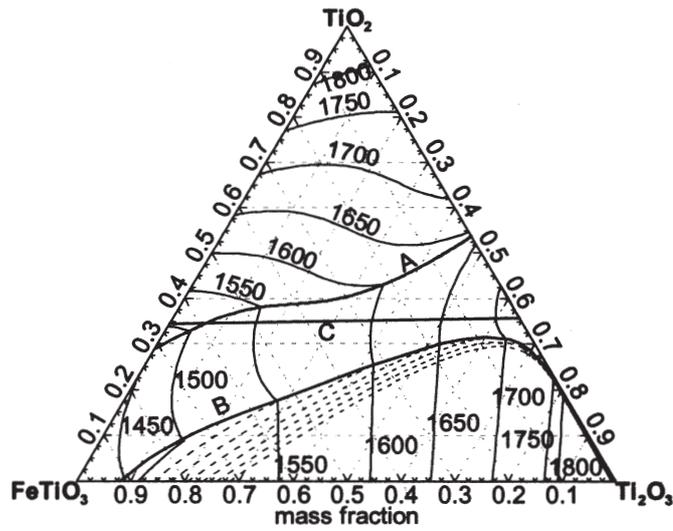† Department of Materials Science and Metallurgical Engineering, University of Pretoria, Pretoria, South Africa.

Figure 1—Liquidus diagram for the TiO₂-FeTiO₃-Ti₂O₃ system excluding Magnéli phases. Broken lines indicate isothermal slag/(slag + Fe°) boundaries. Line A indicates the position of the eutectic groove, Line B the non-isothermal slag/(slag + Fe°) boundary, and line C the M₃O₅ composition

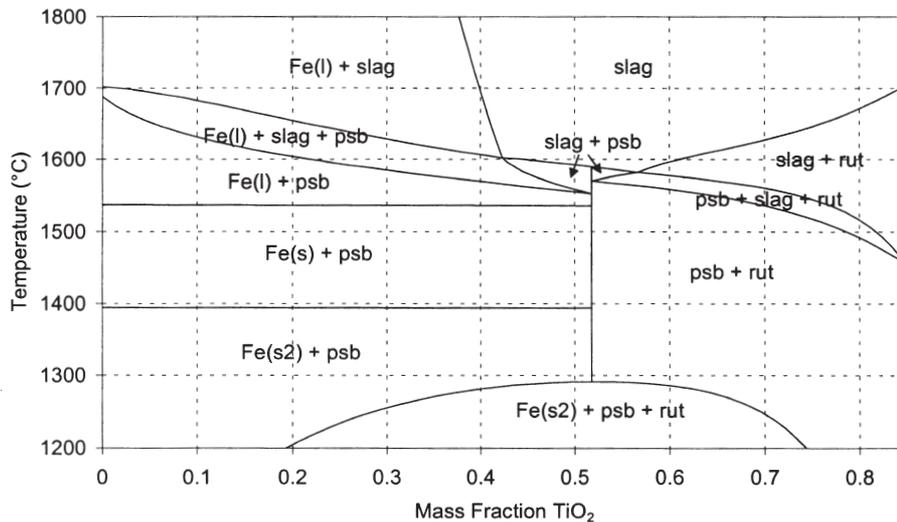

Figure 2—Constant-FeO pseudobinary section through the TiO₂-FeO-Ti₂O₃ ternary phase diagram. 'rut' = rutile solid solution phase. 'psb' = pseudo-brookite solid solution phase (M₃O₅). Mass percentage of FeO = 15.0
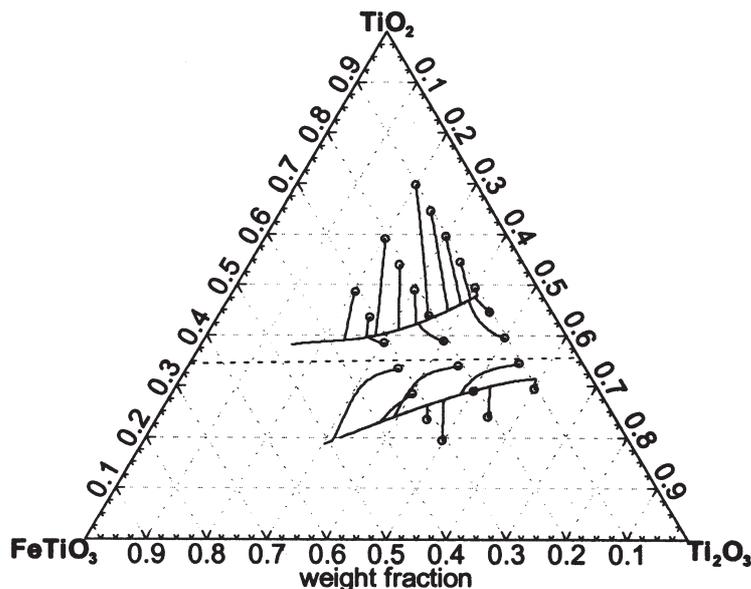
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Figure 3—Liquid slag composition trajectories during solidification. The dotted line indicates the Ti_3O_5-$FeTi_2O_5$ join. Initial composition indicated by circles and trajectories by solid lines

The relationship between FeO and Ti_2O_3

The previously identified[1] relationship between FeO and Ti_2O_3 in industrial high-titania slags is illustrated by Figure 4 and Figure 5. Note that the FeO-Ti_2O_3 relationship differs for slags produced from South African and Canadian ilmenites. The most important difference between these ore types is the significantly higher alkali earth content of Canadian ilmenites[2]. However, slags from both sources follow a single relationship between the divalent and trivalent cation concentrations, as illustrated by Figure 5; in this figure, the divalent cations Mg^{2+}, Mn^{2+} and Fe^{2+} are considered together as a group, and similarly the trivalent cations (V^{3+}, Cr^{3+}, Al^{3+} and Ti^{3+}).

Possible origins of the compositional relationship were previously broadly identified as reaction equilibrium, kinetic effects and phase chemistry[2]. These possibilities are reviewed below.

Reaction equilibrium as a possible mechanism

The high temperatures (around 1700°C) in the smelting furnace and the significant stirring in the slag and metal baths both favour an approach to equilibrium during ilmenite smelting. However, as Figure 1 shows, equilibrium between the iron bath and the slag is reached at significantly lower TiO_2 levels (and hence higher FeO and Ti_2O_3) than M_3O_5 stoichiometry requires—the actual slags contain both lower FeO and lower Ti_2O_3 than equilibrium would require. This is also reflected in a difference between measured and equilibrium oxygen activities[8]. These observations seem to negate virtually all arguments in favour of thermodynamic equilibrium controlling the FeO-Ti_2O_3 relationship.

Kinetic effects as a possible mechanism

It has previously been suggested that the relative reaction kinetics of the reduction of FeO to Fe, and TiO_2 to Ti_2O_3, may govern the extent to which the slag compositions deviate

from equilibrium[1]. Very little is known about the kinetics of reduction reactions taking place in an ilmenite-smelting furnace. However, there are several arguments against kinetic effects as a possible mechanism[2]: firstly, the FeO-Ti_2O_3 relationship is remarkably consistent for furnaces with significantly different sizes and stirring patterns; secondly, the fact that TiO_2 occurs in much higher concentration in the slag compared with FeO, makes it unlikely that a mass transfer limitation would cause lower relative reduction rates of TiO_2; and finally, it is difficult to explain, on the basis of kinetics, why Canadian ilmenites show a consistently lower Ti_2O_3 content at a specific FeO content. As stated in the previous section, the high temperatures and strong mixing in the furnace reduce the likelihood of kinetic effects being responsible for the FeO-Ti_2O_3 relationship. (Note that the Ti_2O_3, which is considered here, is present in solid solution in the M_3O_5 phase, and is not a separate phase.)

Eutectic groove phase equilibrium as a possible mechanism

It was suggested that the presence of a freeze lining in the furnace and the resulting influence of the solidification equilibrium between the liquid slag bath and the solid slag of the freeze lining may be the cause of the FeO-Ti_2O_3 relationship.[3] This suggestion is supported by the observation that this relationship differed in cases where a freeze lining was absent[9]. According to this view, the eutectic groove that is close to the M_3O_5 stoichiometric line (see Figure 1) could serve to constrain the slag composition close to the M_3O_5 composition, with the slag containing slightly more TiO_2 than M_3O_5 stoichiometry requires. This is the case for South African ilmenites[2] (see, for example, Figure 5). In addition, rutile is present in the solidified slag, as would be expected for slag compositions along the eutectic groove (although the actual rutile content of the slags is smaller than expected for compositions along the eutectic groove)[3].
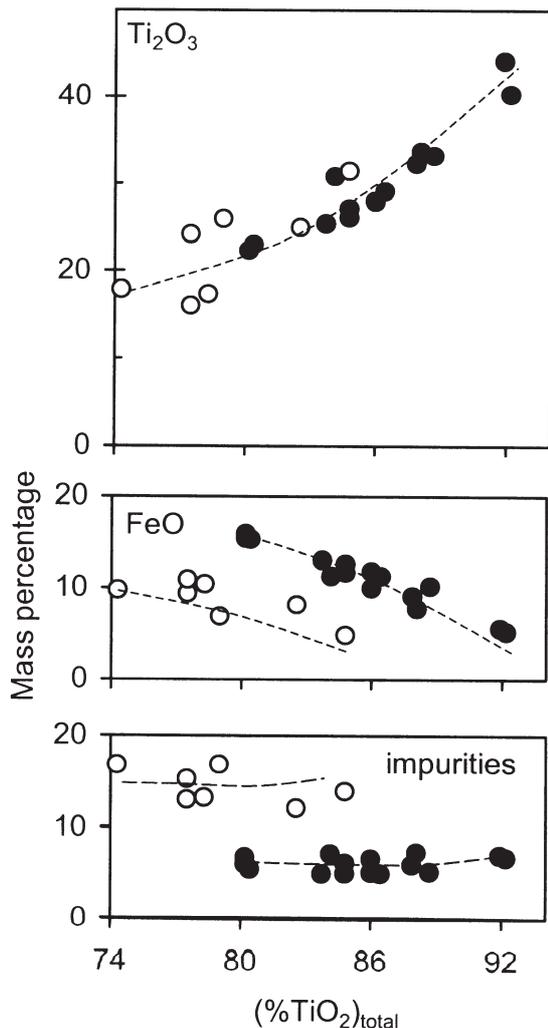
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Figure 4—Compositional relationships in industrial high-titania slags. Filled circles indicate slags from South African ilmenites and empty circles slags from Canadian ilmenites. The horizontal axis indicates the total Ti content of the slag, expressed as TiO_2. Redrawn using previously compiled data[2]

However, the conclusion of a test of the proposed mechanism—using a simple heat transfer model[5]—was that the phase equilibrium between the freeze lining and liquid slag cannot serve to constrain the liquid slag composition to the eutectic groove.

Why would this mechanism not be able to produce the observed FeO-Ti_2O_3 relationship? The most basic explanation is that partial solidification cannot give a lasting change to the composition of the liquid slag: the slag composition does move towards the eutectic groove as a result of partial solidification (see Figure 3), but sustained solidification is incompatible with a constant freeze lining thickness. The only way in which solidification can constrain the slag bath composition close to or on the eutectic groove would be if the products of partial solidification were removed from the furnace continuously. This does not, of course, happen in reality.

A new mechanism proposed

This section describes the details of a new mechanism that is suggested to contribute to the observed FeO-Ti_2O_3 relationship. Any proposed mechanism must meet two basic
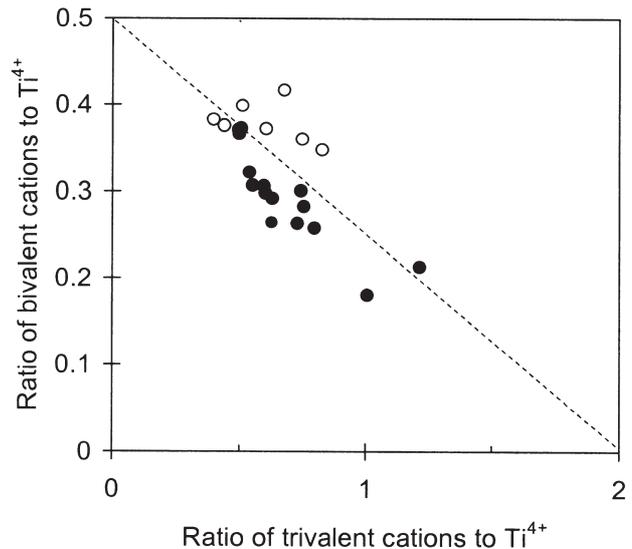

Figure 5—The relationship between divalent and trivalent cations in industrial high-titania slags. Filled circles indicate slags from South African ilmenites and empty circles slags from Canadian ilmenites. Molar ratios are shown. The dashed line indicates the stoichiometric M_3O_5 composition. Redrawn using previously compiled data[2]

requirements:

➤ The mechanism must be able to have a sustained influence on the composition of the slag bath (keeping the slag composition constant while ilmenite and reductant are continuously fed to the furnace and reacting).
➤ The mechanism must be able to adjust the composition of the slag bath towards the stoichiometric M_3O_5 line.

Solidification and disproportionation

In addition to the information on the predicted solidification behaviour of the $FeTiO_3$-TiO_2-Ti_2O_3 system as presented in Figure 1, Figure 2 and Figure 3, additional relevant equilibrium calculation results are given in Figure 6. This figure shows the average composition of the oxidic fraction of initially liquid FeO-TiO_2-Ti_2O_3 combinations after complete solidification. Clearly, all initially liquid slag compositions which lie above the stoichiometric M_3O_5 line remain unchanged in average composition after solidification (giving M_3O_5 and rutile in the solid product). In contrast, the oxidic portion of all liquid slags with initial compositions below the M_3O_5 line reach the M_3O_5 line upon complete solidification. As Figure 2 indicates, the mechanism behind this is formation of metallic iron through the disproportionation reaction (Ti_2O_3+FeO ➡ $2TiO_2$ + Fe) that occurs during cooling. This reaction enriches the oxidic fraction in TiO_2, and depletes it of FeO—giving the composition trajectories that are shown in Figure 6.

This disproportionation reaction—which occurs in tandem with formation of solid M_3O_5—is central to the proposed mechanism. The other key element is the observed temperature difference between the slag and metal baths, where the metal bath is up to 150°C cooler than the slag[1,8]—that is, the metal bath is at a temperature below the solidus temperature of the slag. Slag which is transported to the interface with the metal bath, and is cooled to the
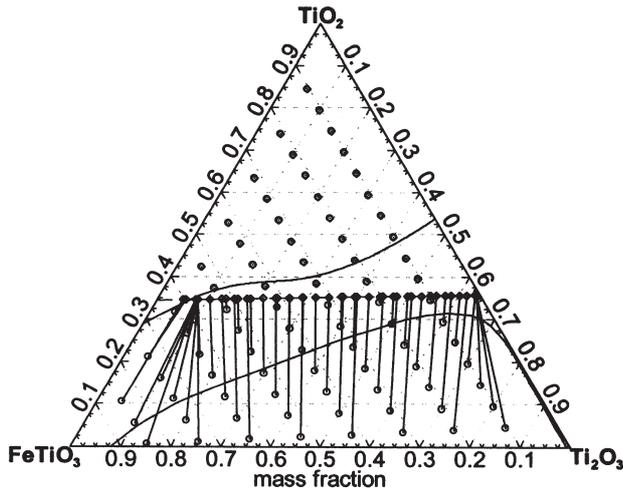
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Figure 6—The influence of solidification on slag composition. A circle indicates an initial liquid slag composition and a diamond the resulting composition of the slag once it had completely solidified. Paired circles and diamonds are connected with solid lines. In most cases slags were cooled to 1400°C. Only the three compositions at approximately 85% FeTiO₃ were cooled to 1300°C

temperature of the metal bath, would hence be transformed to a combination of stoichiometric M_3O_5 and liquid iron. This mechanism is described in detail in the next section.

Description of mechanism

The starting point of the mechanism is an established slag bath with a composition in the vicinity of the M_3O_5 line, indicated by area **A** in Figure 7.

Different reaction steps serve to move the slag composition in different directions from this starting point:

➤ Ilmenite is continuously added to the process. Because of its low melting point (around 1400°C), ilmenite is likely to melt quickly into the slag bath. The influence of ilmenite addition on slag bath composition is indicated by composition vector **A-C** in Figure 7

➤ Reductant is also fed continuously to the process. Reaction between reductant and liquid slag causes the slag composition to be drawn towards area **B** (that is, towards equilibrium with liquid iron). The combined effect of ilmenite addition and reaction towards equilibrium is given schematically by the resultant vector **A-B**

➤ The impinging arc and entering feed material transfer momentum into the slag bath. This stirring contin-

uously circulates slag to and from the interface between the slag and metal baths. As noted above, a significant temperature difference exists between the slag and metal baths, implying that a temperature gradient must exist at the interface between the two baths. This presents a question: Does the transition from the high temperature of the slag bath to the lower temperature of the metal bath occur in a thermal boundary layer in the slag bath, in a thermal boundary in the metal bath, or in thermal boundary layers on both sides of the interface?

Table I shows a comparison of a series of physical properties of molten iron and molten slag. A detailed analysis of these properties and the flow conditions in the furnace is required to provide a final answer to the boundary layer question. However, because the thermal conductivity of slag is estimated to be up to one order of magnitude lower than that of metal, it is proposed that all or most of the temperature transition is located in a liquid slag boundary layer.

Because of the existence of this boundary layer in the slag, the liquid slag circulated to the interface between the slag and metal baths will be cooled. As noted above, cooling causes solidification of slag as pseudobrookite (M_3O_5) with co-precipitation of iron metal. The majority of the precipitated metal is taken up into the metal bath. The solidified slag and the remainder of the metal are circulated back into the hotter bulk slag mass. Under the conditions prevalent in the bulk
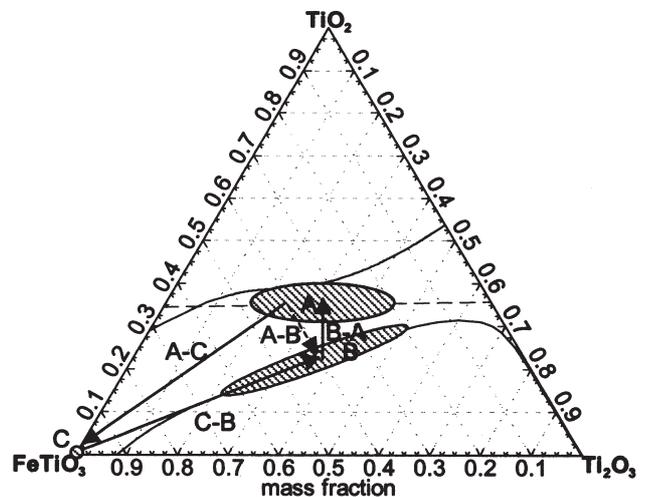

Figure 7—Illustration of the proposed mechanism behind the observed compositional invariance

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Physical properties of molten iron and molten high-titania slag

Symbol	Description	Units	Molten iron	Molten slag
Pr	Prandtl number	none	1.646×10^{-1}	2.974×10^{1}
μ	Dynamic viscosity	kg/(m.s)	7.000×10^{-3} [10]	3×10^{-2} [3]
c_p	Heat capacity	J/(kg.K)	7.170×10^{2} [10]	9.914×10^{2} (FactSage 5.2)
k	Thermal conductivity	W/(m.K)	3.050×10^{1} [10]	1×10^{0} [5]
ρ	Density	kg/m³	7.030×10^{3} [10]	3.800×10^{3} [6]
ν	Kinematic viscosity	m²/s	9.957×10^{-7}	7.895×10^{-6}
α	Thermal diffusivity	m²/s	6.051×10^{-6}	2.654×10^{-7}

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slag, the transiently solidified slag melts and the iron becomes thermodynamically unstable and acts as a reductant converting TiO_2 to Ti_2O_3 and FeO.

The solidification and melting behaviour described above is presented by composition vector **B**-**A** in Figure 7.

Energy balance

An important aspect of the proposed mechanism that needs to be considered is the changes in enthalpy involved with the various steps of the mechanism. To illustrate this, a scenario is described below in which it is aimed to produce a 15% FeO slag situated on the stoichiometric M_3O_5 line. The masses and energy involved in the different steps of the reaction are summarized in Table II; the steps are as follows:

➤ In step 0 ilmenite and reductant (graphite) are added to the system at ambient temperature
➤ In step 1 the ilmenite and graphite are heated to a temperature of 1587°C and allowed to react to equilibrium. This step is endothermic, and produces metal and liquid slag that is lower in FeO
➤ In step 2 the system is cooled to 1553°C, resulting in the release of energy, solidification of slag (as M_3O_5) and precipitation of metal
➤ Finally, the system is heated to 1590°C. This requires 102 kWh/t, transforms the M_3O_5 to the liquid state and precipitates no further metal.

The results indicate that 111.4 kWh per ton of ilmenite is liberated during step 2 when the slag is cooled to its solidus temperature to allow precipitation of iron metal. (In comparison, the overall energy requirement of ilmenite smelting is some 1 MWh per ton of ilmenite, see Table II and reference 1.) This energy—roughly a tenth of the overall energy requirement—must be transferred through the metal bath (by heat losses from the lower sidewalls and hearth) for the metal bath temperature to remain steady. No heat loss data from industrial furnaces are available for comparison.

Test of feasibility

In this section, the proposed mechanism is tested against the requirements stated earlier, and against other factors that could challenge its feasibility.

Firstly, it can be said that a sustained influence is exerted on the composition of the slag bath through this mechanism. This is a result of the circulation of slag to and from the interface between the slag and metal baths, and because of the effectively irreversible nature of the action by which iron is removed from the slag phase and taken up into the metal

bath.

Secondly, the mechanism clearly provides a means of adjusting the composition of the slag bath towards the stoichiometric M_3O_5 line.

The magnitude of temperature changes required by the mechanism is within the known difference in temperature between the slag and metal baths. As Figure 2 indicates, the temperature decrease which is required to change initially liquid slag into a mixture of solid M_3O_5 and iron is predicted to be less than 50°C. However, the nature of the thermal boundary layer at the interface between the two baths is not known; the mechanism depends on a significant portion of the temperature decrease occurring within the slag.

Finally, there is doubt about whether the heat liberated through the cooling step of the suggested mechanism can be removed at a sufficient rate by heat losses through the lower sidewalls and hearth.

If one ignores the uncertainties regarding the thermal boundary layers and the rate of heat removal through heat losses, the proposed mechanism appears feasible. The heat loss rate question should be easy to settle with industrial furnace data.

A reflection on other mechanisms

It is of interest to consider other steps in the process from the basis of the proposed circulation-cooling mechanism.

Reduction reactions in the bulk slag and on the slag bath surface

Firstly consider contact between a reductant particle and slag having a composition in area **A** of Figure 7. Such slag may be found on the surface of the slag bath or in the 'body' of the slag bath away from the turbulent zone underneath the electrode. Initially reduction will only involve the conversion of TiO_2 to Ti_2O_3 since iron metal is not stable under the initial conditions. The composition of the slag in close proximity to the reductant particle must first be changed towards area **B** and the slag/(slag + Fe°) phase boundary where iron metal is able to form. Depending on the rate at which the liquid slag close to the reaction interface with the shrinking reductant particle is being renewed via diffusion and convective mass transfer, the liquid slag in the small system may reach a point of iron metal stability or it may not.

If metal is indeed formed, the produced droplet, or droplets, must somehow find its way to the metal bath. It is

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Table II

Energy and mass balance details of steps in the proposed mechanism

Step	Ilmenite Mass g	Reductant Mass g	Temperature °C	ΔH kWh/t	Slag(l) Mass g	Slag(s) Mass g	Metal Mass Change g	%FeO Content Mass%
0	100	7.96	25	–	–	–	–	47.35
1	–	–	1587	916.3	60.88	–	28.40	17.84
2	–	–	1553	-111.4	–	59.36	1.52	15.01
3	–	–	1590	102.0	59.36	–	0.00	15.01

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likely that, during this travel, it will come into contact with liquid slag that is representative of the bulk conditions (composition in area **A** and temperature close to the bulk slag temperature) in the slag bath. According to the available thermodynamic data, the carbon in the metal droplet will first react with TiO_2 to form Ti_2O_3 and CO gas. This leaves a virtually pure iron droplet. Under the bulk slag conditions iron is not stable. It will react with TiO_2 to produce Ti_2O_3 and FeO.

It therefore seems that iron produced by reduction reactions between liquid slag and reductant, is unlikely to eventually be taken up into the metal bath if it has to travel through the bulk slag to reach the metal bath.

Reduction reactions at the interface between the slag and metal baths

The metal bath in an ilmenite smelter contains some 2% carbon, which can also contribute to reduction. However, if the circulation-cooling mechanism operates, reaction between the high-carbon metal and slag will be inhibited for two reasons.

Firstly, the metal at the interface will be enriched in Fe—diluting the carbon content—because of the newly precipitated metal. Secondly, the slag at the interface will be at least partly solidified. The rate of reaction between liquid metal and solid slag is likely to be significantly lower than reaction between liquid metal and liquid slag.

Reduction reactions in the turbulent zone beneath the electrode

Conditions and reactions in the zone beneath the electrode (in a DC smelter) are highly uncertain. However, a number of general observations can be made:

The local slag composition in this zone is likely to be drawn relatively far towards zone **C** in Figure 7 because of ilmenite entering through the electrode. It is likely that at least some reduction takes place in this zone due to the high temperatures and the presence of reductant particles. It is also likely that, because of the local slag composition, a significant amount of iron metal is formed as a result of the reduction reactions.

Carbon dissolution

One phenomenon in the ilmenite-smelting process that is not yet understood clearly is the transfer of carbon into the metal bath. As noted above, a metal carbon content of around 2% has been observed in ilmenite smelting processes[8]. This is far from the composition for metal in equilibrium with slag (which is less than 0.2% according to simple FactSage equilibrium calculations). At least two possible phenomena can contribute to maintaining the carbon content of the metal above equilibrium. Firstly, in the turbulent zone underneath the electrode liquid metal droplets may come into contact with reductant particles. It is not certain what the typical temperature in this region is, but with slag being tapped at temperatures in excess of 1700°C, it is likely that the temperature of the zone underneath the electrode could be substantially higher. The carbon solubility in liquid iron is

relatively high at these temperatures—ranging from 5.7% at 1700°C to 5.9% at 1800°C.[11] Substantial carburization of liquid iron is hence possible here, and where metal droplets from reduction reactions at the slag-reductant interface contact solid carbon. However, such droplets will tend to lose carbon by reaction with the slag while travelling through the slag bath.

The equilibria of the opposing reactions of carburization of the metal through contact with reductant, and decarburization through reaction with the slag, do lie on either side of the actual bath composition. However, data from industrial smelters (on, for example, the carbon content of droplets beneath the electrode, and elsewhere in the slag bath) would be required to decide the relative importance of these reactions. If the metal droplets which travel through the slag do react to equilibrium, such droplets would not only be decarburized, but the metallic iron would also be oxidized to FeO. In such a case, all the carbon reaching the metal bath would have to be transferred in the region below the arc.

Conclusion

It is proposed that a combination of thermochemical equilibrium and transient cooling and solidification of liquid slag at the interface between the slag and metal baths, followed by re-melting of the solidified slag, strongly contributes to the observed compositional invariance of industrial high-titania slag close to the stoichiometric M_3O_5 composition. This mechanism can exert a sustained influence on the composition of the slag bath towards the M_3O_5 composition. The temperature differences between the slag and metal baths that are required by the proposed mechanism agree well with temperature differences found in reality.

Uncertainties include the nature of the thermal boundary layers between the slag and metal baths, and the capacity of losses from the lower sidewalls and hearth to remove heat liberated by the proposed mechanism. These aspects need to be investigated to further test the feasibility of the proposed mechanism.

Conditions and mechanisms in the zone underneath the arc remain uncertain. However, it is expected that iron is produced at a significant rate in this zone, and that most of the carbon present in the metal phase reaches this phase via metal–reductant contact in the turbulent zone underneath the arc. Carbon transfer into metal as a result of reduction reactions between slag and reductant seems less likely, based on thermodynamic considerations.

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