



Reductant selection in ferro-alloy production: The case for the importance of dissolution in the metal

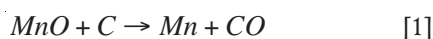
by P.C. Pistorius*

Synopsis

The typical reactions which the reductants undergo during ferroalloy production are reviewed, and identified as reaction with CO₂ and with SiO₂, and dissolution in metal. Available reactivity tests for these three reactions are reviewed. It is proposed that it is worthwhile considering dissolution kinetics as a reactivity parameter. Greater crystallinity of the reductant decreases CO₂ and SiO₂ reactivity, but increases dissolution rates.

Introduction

In the production of ferroalloys in submerged-arc furnaces, the primary function of the carbonaceous material (mainly coke and coal) is to act as reductant: to react with the metal oxide to form metal and carbon monoxide. For example, in the production of ferromanganese the overall manganese reduction reaction can be written as



Standard free energy changes for the reduction of Cr₂O₃, MnO, SiO₂ and FeO by carbon are shown in Figure 1. Figure 1 suggests that the only real condition for the carbothermic reduction of these oxides is to heat the oxide-reductant mixture to a high enough temperature. Viewed in this simplistic way, the only requirement of a reductant for ferroalloy production (apart from the requirement that the reductant must contain carbon!) would be that it has an acceptably low level of impurities (such as sulphur and phosphorus) which would otherwise contaminate the product. While the chemical composition of the reductant is no doubt important¹, the practical use of a mixture of reductants and of considerable amounts of relatively expensive coke indicates that there is more to the choice of reductant than simple compositional considerations. (Typically, 40% of the reductant is coke in the case of ferrochromium production, with the cost of the reductant sometimes more than that of the chromite ore¹.)

The reasons for choosing reductants based on more than composition arise from the actual steps which make up the overall reduction reaction, and from the electrical function. These are briefly reviewed below.

Reaction steps in ferroalloy production

The reaction sequences in the production of ferromanganese, ferrosilicon and ferrochromium were well studied in a remarkable series of local projects, mainly in the late 1970s³⁻⁸. I cannot give justice to the full range of that work here. Rather, I restrict myself to summarizing the reactions which the reductant is likely to undergo. While this paper aims to identify general themes, it is clear that the reaction sequences in the production of different ferroalloys are quite different, and hence I mention these under separate headings (covering only three ferroalloys which I consider typical).

Ferromanganese

Excavation of a 75 MVA furnace following shutdown and water quenching^{5,6} revealed several different reaction zones within the furnace (Figure 2). In the upper part of the 'reaction cone' around the electrodes, gaseous reduction (by CO) of mainly the FeO in the ore occurs, yielding porous ore particles containing solid metallic iron. Formation of a primary slag temporarily halts this reaction. Reduction resumes at higher temperatures, through reaction with carbon dissolved in the metal, and—lower in the furnace—with solid carbon. Based on the analogous reactions in iron production, it appears likely that reaction of slag with solid carbon in fact occurs via the gaseous intermediates CO and CO₂⁹.

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

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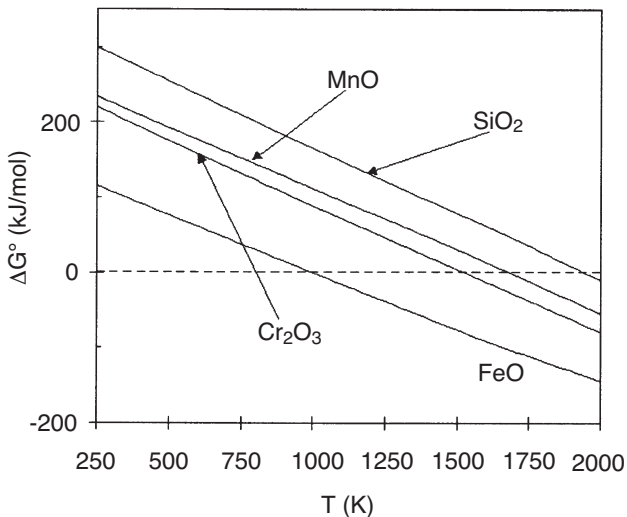


Figure 1—Standard free energy change for the reduction of the indicated oxides with carbon, yielding the metal and CO as products. Calculated with the FACT database². The free energy change is given per mole of atomic oxygen

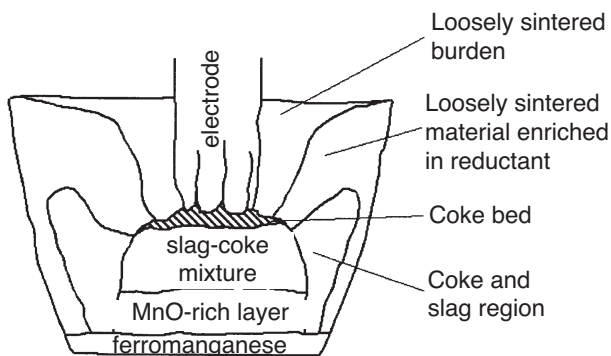


Figure 2—Cross-section through excavated ferromanganese furnace, showing the part of the furnace within the lining (not shown) at a vertical section through one of the electrodes (drawn after Barcza *et al.*⁴)

The actual ways in which the reductant takes part in the reduction reactions are, hence:

- ▶ gasification (presumably by the Boudouard reaction*) to form CO which can react high in the furnace
- ▶ dissolution of carbon in the metal product
- ▶ reaction of the dissolved carbon with MnO in the slag as the metal descends to the hearth ('metal refining')
- ▶ gasification by the Boudouard reaction as part of the 'direct reduction' reaction of solid carbon with MnO in the slag.

Ferromanganese

While there is some reduction of iron in the solid state (with CO as the reductant),^{3,10} the reduction rate apparently only increases strongly once the chromite starts dissolving in the slag above 1500°C;³ the reduction reaction then occurs through reaction of dissolved chromium oxide in the slag

*The Boudouard reaction is: $CO_2 + C \rightarrow 2CO$

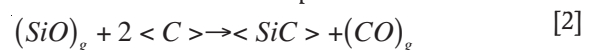
with solid carbon, or with carbon and silicon dissolved in the metal¹¹. The silicon content of the metal increases as the material approaches the high-temperature region ('coke bed') close to the electrode tips¹¹. The regions found in a quenched experimental furnace¹¹ are somewhat similar to those shown for the ferromanganese furnace (Figure 2).

The relevant reactions of the reductant can be summarized as follows:

- ▶ dissolution of carbon in the metal product
- ▶ reduction of silicon (presumably by production of SiO gas in the higher-temperature region, with reduction of SiO to silicon or silicon carbide higher in the furnace)
- ▶ reaction of dissolved carbon with Cr₂O₃ in the slag as the metal descends to the hearth
- ▶ gasification by the Boudouard reaction (during direct reduction).

Ferrosilicon

In the production of silicon or ferrosilicon, it appears that the major gaseous reagent is silicon monoxide (SiO), which can form through the reaction of silicon or silicon carbide with SiO₂ in the high-temperature region of the furnace⁷. The SiO product rises through the furnace and reacts with the reductant in the upper part of the furnace, to yield silicon carbide and carbon monoxide as products⁷:



According to this mechanism, the only major reaction of the reductant is with SiO gas.

Summary of reductant reactions

From this brief overview, it appears that the solid reductant undergoes several quite different reactions during ferroalloy production:

- ▶ Boudouard reaction (ferromanganese and ferrochromium)
- ▶ dissolution in the metal (ferromanganese and ferrochromium)
- ▶ reaction with SiO (ferrosilicon and likely ferrochromium).

Ways of testing the reactivity of the reductant in these very different reactions are reviewed next.

Reactivity tests

The main tests for the three types of reactivity are described below, with typical trends of reactivity with reductant type.

CO₂ reactivity

A common test for blast furnace coke is the exposure—of a packed bed containing 200 g of 20 mm-diameter particles—to flowing CO₂ at 1100°C for 2 hours¹². The percentage mass lost (by the Boudouard reaction) is quoted as the 'coke reactivity index' (CRI). The extent of size degradation is quantified by determining the percentage of the remaining coke (after reaction and tumbling) which is larger than 10 mm; this percentage is quoted as the 'coke strength after reaction' (CSR). The CRI and CSR values are generally inversely related, indicating that the loss of strength in this test is a direct result of reaction¹³.

High CSR values are important in the iron blast furnace: coke strength is essential to the maintenance of furnace

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permeability, given the high gas flow rate in blast furnace ironmaking. Because of this importance, several correlations were developed to predict the CSR of coke prepared from coal blends. For example, in the Inland Steel approach¹⁴, combining the coal plasticity (as determined with the Gieseler plastometer) and the 'catalytic index' (CI) yielded the best results—coals or coal blends with higher plasticity values and lower catalytic indices have higher CSR values. The catalytic index is calculated from the composition of the coal ash and the coal sulphur content:

$$CI = 9.64(CaO + MgO + Fe_2O_3 + Na_2O + K_2O) / [3] (SiO_2 + Al_2O_3) + 14.04(S)$$

This expression aims to account for the catalytic effect of some oxides (notably, iron oxide and CaO) on the reaction with CO₂. The strong effects of iron oxide and free lime to increase coke reactivity were also illustrated in work where various minerals containing these compounds were added to the coal mixture before coking¹⁵.

While it is feasible to predict and measure the CRI and CSR, it is not obvious what values of these indices are desirable for coke used in ferroalloy production: given the apparent importance of CO generation (in direct reduction reactions), it appears that a high reactivity/low CSR would be required. On the other hand, the primary electrical contact between the electrode and the charge is through a 'coke bed' directly beneath the electrode tips (see Figure 2)^{4,11}. Use of a less reactive coke would presumably favour maintenance of such a coke bed: smaller-sized and more-reactive coke is stated to give higher resistivity¹⁶.

These counteracting requirements perhaps partially explain the general use of a mixture of reductants in ferroalloy production. In general, higher-rank coals and coke have lower CO₂ reactivity than lower-rank coals and charcoal.

SiO reactivity

When a carbonaceous reductant reacts with SiO, solid silicon carbide forms, as shown in reaction [2]. This silicon carbide eventually blocks the reaction surface. It appears that the rapidity of the onset of surface blockage can be used as an indication of reactivity with respect to SiO (the onset of blockage is indicated by a decrease in the concentration of CO in the off-gas from a reactor in which the reductant reacts with SiO at 1650°C; CO is a product of the reaction of SiO with carbon—reaction [2])⁷. In general, the trend of SiO reactivity with reductant type is similar to CO₂ reactivity: charcoal and lower-rank coal are more reactive than coke and higher-rank coal. Although the high reactivity of charcoal with SiO would make charcoal attractive for the production of silicon, it was found that this reductant generated fines when its surface was converted to silicon carbide—a compromise between reactivity and strength retention is thus required⁷.

Dissolution rate

A great deal of work has been performed in recent years by the group of Sahajwalla to characterize the dissolution rate of reductants in iron-based hot metal^{e.g.17–20}. Dissolution rates were measured experimentally by placing a cover of the relevant reductant on molten iron (initially containing 2% C) in an induction furnace at 1550°C, and monitoring the

carbon increase in the iron. The carbon increase was assumed to follow the simple first-order rate equation

$$d[\%C]/dt = K([\%C]_{sat} - [\%C]) \quad [4]$$

where [%C] is the carbon content at a given time, [%C]_{sat} is the carbon solubility in the melt, and *K* is the apparent rate constant.

It was found that the coal property affecting the dissolution rate most strongly is the degree of crystallinity. One model of the complex structure of coal is that it consists of small regions which have the graphite crystal structure, with complex three-dimensional bonds between these ordered regions (Figure 3)²¹. A measure of the degree of crystallinity of the coal is then the average thickness of the ordered regions (crystallites); this average thickness can be measured by using the peak broadening effect in X-ray diffraction (XRD) measurements. Higher-rank coals exhibit narrower peaks in the XRD spectrum, and hence have larger crystallites²¹. Contrary to the behaviour regarding CO₂ and SiO reactivity, the more crystalline coals or chars exhibited more rapid dissolution (Figure 4)—perhaps because the complex three-dimensional bonds in poorly ordered coal are more difficult to break²⁰ (Figure 4).

All of these results are based on dissolution in iron-based hot metal, sometimes with controlled sulphur additions (as expected, sulphur decreases the dissolution rate). It is not known how dissolved chromium, manganese and silicon affect the dissolution rate and the role of coal structure.

Conclusions

At least three different reactivity properties of reductants are

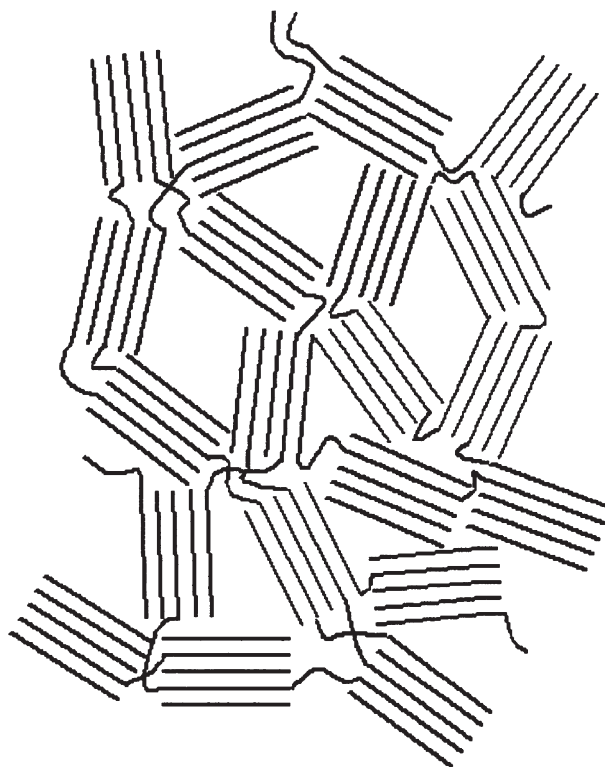


Figure 3—Schematic of the proposed structure of coal, consisting of crystallites with graphite structure, surrounded by an unordered matrix. Drawn after van Krevelen²¹

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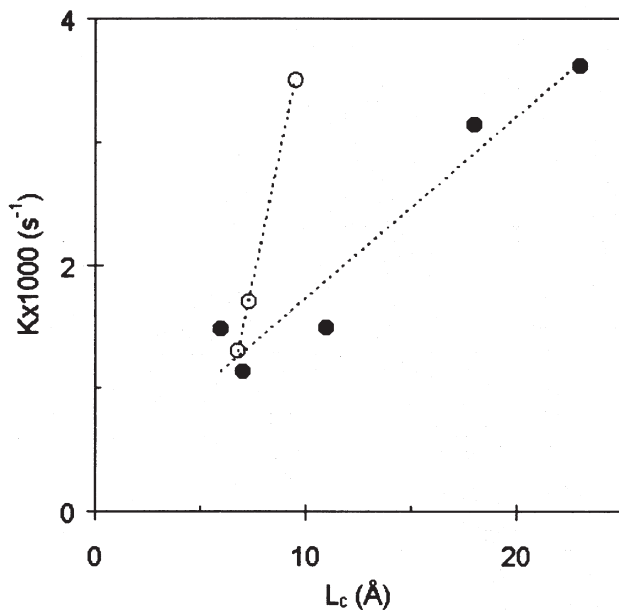


Figure 4—Rate constant for the dissolution of carbon in iron at 1550°C, for coals with different crystallite sizes (L_c) (filled circles), and for a single coal charred at increasingly higher temperatures to yield larger values of L_c (open circles). Redrawn from the data of Sahajwalla *et al.*²⁰

important in ferroalloy production: CO_2 reactivity, SiO reactivity, and dissolution rate in the metal. While the first two appear well-established in current practice, it seems worthwhile to investigate the validity of dissolution kinetics as an additional technical reductant selection criterion.

Acknowledgement

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