



Ore size does affect direct reduction of titaniferous magnetite

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Synopsis

This work tested whether ore particle size affects the carbon-based pre-reduction of titaniferous magnetite. Pre-reduction is performed at a temperature of some 1100°C in a rotary kiln, in the Highveld Steel process. Laboratory isothermal reduction measurements were performed with ore-coal mixtures at this temperature, to test the effect of ore particle size. The results show that size does limit the degree of reduction for particles larger than 15 mm.

Background

In the Highveld Steel process,¹ titaniferous magnetite (which also contains a substantial amount of vanadium) is pre-reduced in a rotary kiln, using coal as reductant. The residence time in the furnace is some six hours, and about 50% metallization of the iron is achieved in the kiln. Pre-reduction serves to decrease the energy requirement during subsequent electric smelting of the charge. The extent of pre-reduction affects the energy requirement and carbon balance during electric smelting, and hence a stable and high degree of pre-reduction is advantageous.

Previous work indicated that the rate of pre-reduction is controlled by the coal gasification (Boudouard) reaction.² However, this conclusion was based on laboratory measurements with ore particles of approximately 6 mm in diameter. The feed to the rotary kiln can contain pieces of ore that are up to 50 mm in diameter. For large ore particles, diffusion of the reduction gas (mainly CO) through the iron product layer into the particles—and the diffusion of the reaction product (CO₂) in the opposite direction—may limit the reduction rate. For full diffusion control, the effect of ore size is strong, with the time for a given degree of reduction being proportional to the square of the particle diameter.³

Experimental work

A sample of titaniferous magnetite ore, from

the feed to the rotary kiln, was received from Highveld Steel and Vanadium, together with a sample of the coal used as reductant. The ore samples were prepared for reduction experiments by screening the ore into ten size fractions (ranging from -8 mm to -70+50 mm), and the coal by devolatilizing at 900°C. Ore samples from the different size ranges were analysed by X-ray fluorescence (XRF) and X-ray diffraction (XRD), and polished sections examined by scanning electron microscopy with energy dispersive micro-analysis (SEM/EDS). These showed that all size fractions consisted largely of magnetite, with a slightly higher gangue content in the smaller ore particles.

Based on the analyses, and assuming that chromium and vanadium are present in the magnetite in only the trivalent form, and that all titanium is tetravalent, the average composition of the magnetite is approximated by $\text{Fe}_{1.0}^{3+} \text{Fe}_{1.3}^{2+} \text{Ti}_{0.39}^{4+} \text{Al}_{0.13}^{3+} \text{Mg}_{0.09}^{2+} \text{V}_{0.06}^{3+} \text{Cr}_{0.01}^{3+} \text{O}_4$.

Reduction experiments were performed by maintaining ore-coal mixtures at 1100°C in a vertical tube furnace, under an argon atmosphere. The mixtures were made up by using different ore size fractions, whereas all the coal particles were approximately 6 mm in diameter. The mass ratio of ore to coal in the mixture was 2.9:1. Each mixture was contained in an alumina crucible with an inner diameter of 50 mm; the crucible was suspended in the hot zone of the furnace for reduction. Following reduction for different lengths of time, the crucible was lifted from the hot zone, and cooled under argon. Coal particles were separated from reduced ore particles by hand, and the mass loss of the ore determined to give a measure of the degree of reduction. Most samples were reduced for up to 6 hours.

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Thermocouple-based temperature measurements close to the centre of a few samples showed that the sample reached the set furnace temperature within 1 hour, which is a short period compared with the total reduction time; this means that reduction was not limited by heat transfer into the packed bed under these experimental conditions.

Results and discussion

Reduction mechanism

Examination of partially and fully reduced samples by XRD and SEM/EDS showed that reduction occurred in two steps. In the first step, the magnetite was converted to a mixture of wüstite ('FeO') and ulvöspinel (with the approximate composition Fe_2TiO_4). This first reduction step appeared to occur uniformly throughout the ore particles, and is hence not significantly affected by particle size. Based on the original composition (as given above), this step involves a mass loss of 3.7% (relative to the original ore mass), and a percentage reduction (based on the decrease in the amount of oxygen associated with iron) of 18%.

In the second reduction step, the wüstite which formed during the first step was reduced to metallic iron. For the larger ore particles, a product layer formed in the outer regions of the particles, with unreduced cores (of wüstite and ulvöspinel) in the centre. This is the expected morphology if gaseous diffusion through the product layer limits the rate of reduction. Full reduction of the wüstite to metallic iron implies a total mass loss (relative to the original ore mass) of 15%, a percentage reduction (based on oxygen associated with iron) of 72%, and a percentage metallization (that is, the percentage of the iron which is present in the metallic form) of 66%.

No reduction of the ulvöspinel occurred even after extended exposure of the samples at 1100°C with unreacted carbon present in the samples. This implies that the maximum degree of metallization that is achievable during pre-reduction is limited by the Fe:Ti ratio in the ore: with a higher titanium content in the ore, more iron would be captured in ulvöspinel, with a correspondingly lower

maximum degree of metallization. For the ore used in this work, the Fe:Ti ratio was approximately 6.0. This means that, out of every 6 moles of iron that are present in the original ore, approximately 2 moles would be captured in ulvöspinel (Fe_2TiO_4) and a maximum of 4 moles of iron could be reduced to the metal—a maximum percentage metallization of 67% (this is slightly different from the value of 66% which is quoted above, since the latter value was calculated by taking into account the presence of cations other than Fe^{2+} and Ti^{4+} in the spinel).

This reduction sequence is summarized schematically in Figure 1. Photomicrographs of partially and fully reduced samples are shown in Figures 2 and 3.

Effect of ore particle size

The observation of a reaction product layer around partially reduced cores suggests that gaseous diffusion limited the reduction rate, which implies that ore particle size should affect reduction. This is confirmed by the results in Figure 4, which give the mass loss of the ore as a function of size. (The sizes plotted in this figure are the averages of the sieved size ranges, which were used in the different runs.) Clearly, larger ore particles show significantly lower mass losses (which correspond to lower degrees of reduction).

Based on the discussion on the reduction mechanism, the maximum mass loss—for full reduction to metallic iron and ulvöspinel—is some 15%. However, the smaller ore particles showed larger mass losses, of up to 18.5% (Figure 4), even though no reduction of iron from the ulvöspinel could be detected by electron microscopy. The likely reason for the larger mass losses of the smaller-sized fully reduced particles is that their composition was slightly different: the molar ratio Fe:Ti in the smallest size range was 6.2, which is larger than for the larger size range. This means that less iron is captured by the ulvöspinel, and hence a larger degree of reduction is possible.

Conclusion

Carbon-based direct reduction of titaniferous magnetite does

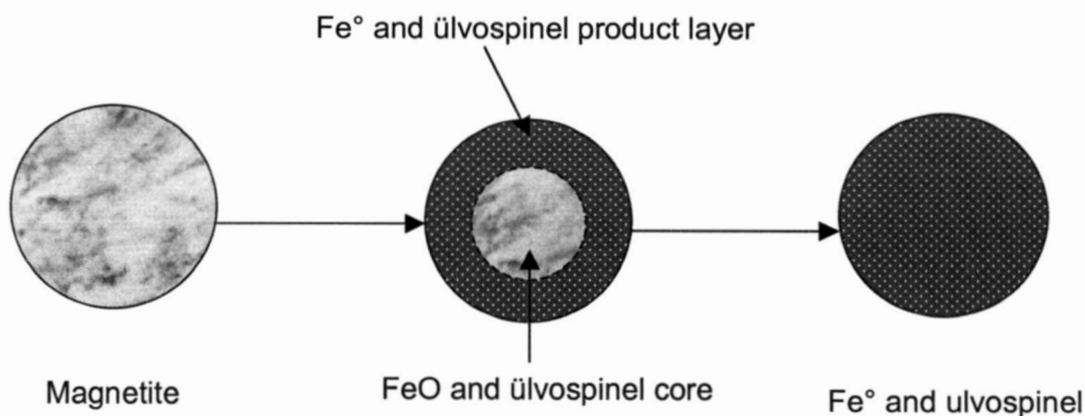


Figure 1—Schematic of the reduction sequence of titaniferous magnetite, during direct reduction

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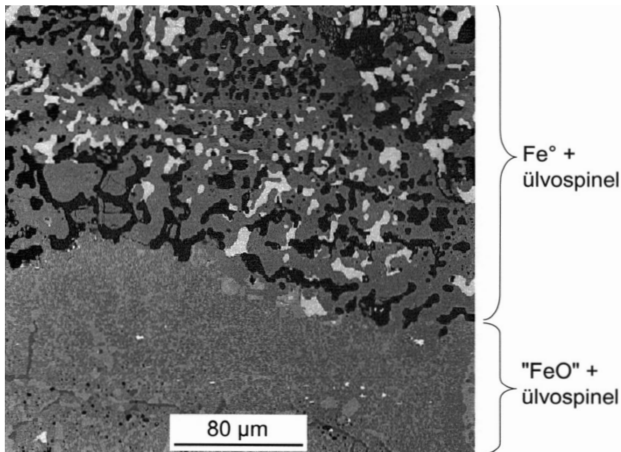


Figure 2—Reaction front region on a cross-section through partially reduced titaniferous magnetite, showing the partially reduced core (consisting of wüstite— FeO° —and ülvospinel), and the product layer (consisting of metallic iron and ülvospinel). The product layer is in the upper part of the image, and the partially reduced core in the lower part. Scanning electron micrograph (back-scattered electron image)

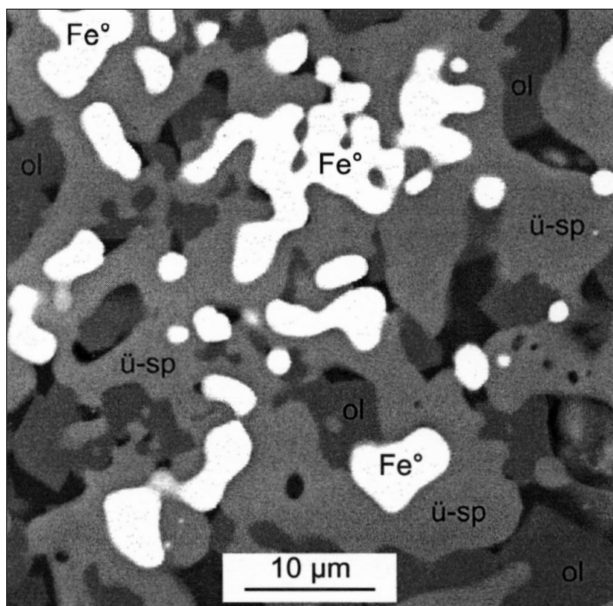


Figure 3—Cross-section through fully reduced titaniferous magnetite, showing the main phases to be metallic iron (labelled with Fe° in the micrograph), ülvospinel (ü-sp), and olivine (ol)

depend on particle size: for the typical residence time and kiln temperature of 6 hours at 1100°C , ore particles larger than 15mm in diameter are not fully reduced. The degree of reduction is also limited by the formation of ülvospinel,

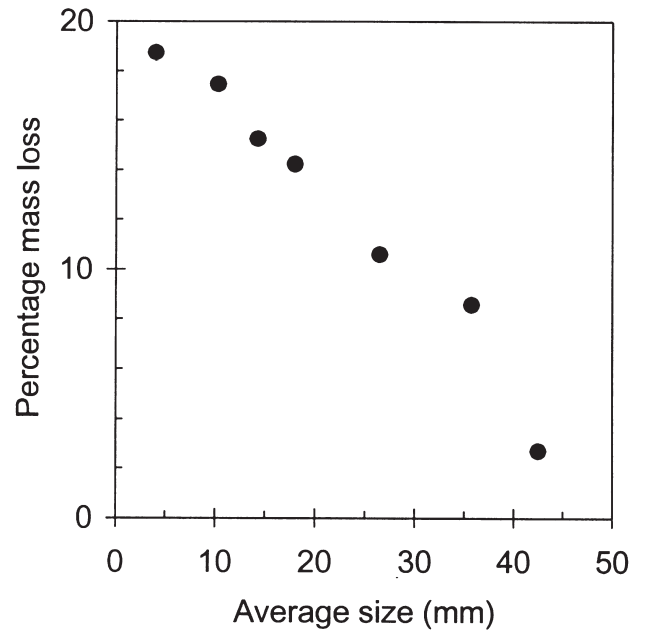


Figure 4—Effect of ore particle size on the mass loss after 6 hours of coal-based direct reduction at 1100°C . Particles smaller than 15 mm are fully reduced (mass loss of 15% or more)

which captures some of the iron in an unreducible form; ülvospinel formation limits the maximum achievable metallization to some 66%.

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Tin market expected to be in deficit until at least

New report analyses tin supply and demand worldwide

In 2004, tin performed the best of the six base metals traded on the LME, with prices increasing by almost 150% between August 2002 and May 2004, according to a new report from market analyst Roskill. Tin's market strength is underpinned by increasing demand, stagnant supply and low inventories, meaning that the market is expected to be in deficit until the end of 2005, with a shortfall of around 15 kt in 2004.

The Economics of Tin (8th Edition, 2004) explains that the fundamentals of the tin market point to continued strength well into 2006, with the price remaining between US\$ 8 000 and US\$ 9 500/t. There is, however, an argument for considerably higher prices should world economies continue to grow at or about the rates seen in 2004, and tin supply struggles to keep pace.

Possible revival of tin mining in Malaysia and Thailand

The long period of low tin prices resulted in prolonged under-investment and a decline in the tin mining industries of Malaysia and Thailand, although both countries still have considerable refining capacity. The sharp decline in refined tin production in both of these countries in 2003, probably resulted from the restrictions placed on concentrate exports from Indonesia in 2002.

Since these restrictions on unofficial Indonesian exports have been put in place, companies such as Malaysia Smelting Corporation (MSC) have started to acquire interests in Australian and Indonesian tin mining companies in order to secure future supplies of concentrates. However, Malaysia itself is home to some of the largest known tin deposits, representing about 11% of the world total. Therefore, should the increasing price justify it, there are sufficient resources to sustain a significant expansion of the Malaysian tin mining industry.

Large increase in Chinese demand

China is by far the largest market for tin, and accounts for the bulk of the increase in world demand since 2002. In 2003, Chinese consumption had risen to 24% of the world total, followed by that in the USA (14%) and Japan (9%). Chinese tin consumption is expected to total 80 kt in 2004, reducing exports still further in the absence of any major new production.

Production of tin in China increased from around 20 kt to 112kt between 1985 and 2000 to become the major producer, during a period when production in most other

countries was declining. Production declined in 2002 as the Chinese government enforced its environmental and safety guidelines, which resulted in some twenty thousand small workings being closed. Output recovered in 2003 to 100 kt, but the gap between concentrate production and demand smelters is growing, and the deficit in 2004 was reported to be about 40 kt of tin-in-concentrates.

Solder is now the largest end-use application for tin

The largest end-use application for tin is now in solders, accounting for 36% of total consumption. Tins use in solder, particularly in China where solder alone accounts for 10% of world tin consumption, has grown very rapidly in recent years with the boom in consumer electrical appliances and electronics.

This demand has been greatly enhanced by the move to lead-free solders, backed up by legislation in Europe, Japan and China. Solders that typically contain about 63% tin are being replaced chiefly with solders containing over 95% tin, creating a 35% increase in tin demand (allowing for weight differences) for the same task. The conversion was only about 15% complete in 2004, but is expected to be almost total in Japan and Europe by the end of 2006.

Decline in use of tin in tinplate

The coating of steel for tinplate was once the major end-use application of tin, but now probably ranks after tin chemicals as the third largest use. The tinplate market declined in the 1970s and 1980s, mainly in the USA, but has now stabilized at around 56 kt or 18% of total world consumption.

The single largest use for tinplate, in beverage cans, was taken over completely by aluminium in the USA, though in Europe, Japan and China it still has a major share in the beverage canning market. In addition to aluminium, tinplate competes with plastics and glass in packaging, but is still the dominant material in food and non-food canning. The ease of recycling steel cans has helped to maintain their market share. However, the coating of tin in tinplate has got progressively thinner, and now only makes up about 0.25% by weight of a 33 cl beverage can weighing 22 g.

The Economics of Tin (8th edition, 2004) is available at £1950/US\$3900/EUR3415 from Roskill Information Services Ltd, 27a Leopold Road, London SW19 7BB, England. Tel: +44 20 8944 0066. Fax: +44 20 8947 9568. E-mail: info@roskill.co.uk ◆