Thermochimica Acta, 103 (1986) 181—186
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE HYDROGEN REDUCTION OF IRON ORE SINTERS

F.A. ADEDEJI[1] and F.R. SALE[2]
[1]Delta Steel Complex, Warri, Nigeria.
[2]Department of Metallurgy and Materials Science,
University of Manchester/UMIST, Grosvenor Street, Manchester M1 7HS.

ABSTRACT

The hydrogen reduction of a series of sinters, produced from a Northamptonshire iron ore with various additions of coke, has been investigated over the temperature range 800°C to 1100°C using an electromagnetic balance. The reducibilities varied according to the carbon content of the original mix with high carbon sinters being less reducible than low carbon sinters. This difference was related to the porosities of the sinters and not to the iron-bearing phases present in the sinters. At 1100°C the densification and sintering of the newly-formed metallic iron caused a decrease in reduction rates relative to those achieved at 1000°C.

INTRODUCTION

The use of sinter in blast furnaces has particular benefit in the case of fine grained, dusty ores especially if they are of a lean quality. The conversion of the ore to a sinter allows a strong porous solid to be produced, which is ideal for the gas-solid reactions of the blast furnace. It also allows a number of decomposition reactions to be carried out outside the blast furnace using coke breeze which is a cheaper fuel than the sized metallurgical coke used in the blast furnace. The strength of the sinter is also of prime importance in the blast furnace because a weak material can be broken down in the charging process or inside the blast furnace. This series of experiments was designed to investigate the reducibilities of a series of sinters, made with varying coke breeze additions, to determine whether reducibility was affected by either the degree of oxidation of the sinter or the physical state of the sinter.

EXPERIMENTAL PROCEDURE

Preparation and characterisation of sinters

The sinters were prepared under identical conditions in an experimental sinter box at BSC, Corby. The iron ore to slag-forming components were kept constant to give a basicity of 0.9 for all the sinters. To check this Ca, Mg, Fe, Al and Mn were determined by atomic absorption spectrometry whilst Si was

0040-6031/86/$03.50

determined by a combination of gravimetric and colorimetric methods. The phases present in the sinters and in the products of partial and full reduction were identified by a combination of X-ray diffraction analysis, optical microscopy, scanning electron microscopy and microhardness measurements. The coke levels in the original sinter mixes were 3.5, 5, 6, 7 and 8wt%.

Reduction of the sinters

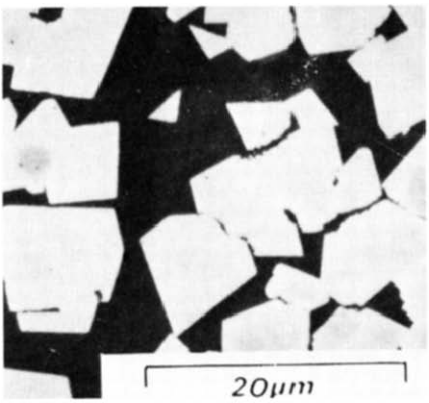
The rates of reduction of the sinters were determined using a CI Electronics 2TC5 electrobalance fitted with a remote vacuum head and universal attachment. Critical flow rate determinations gave a value of 125ml min^{-1} for the hydrogen reduction of the 3.5wt% sinter mix (the most reducible sinter). Consequently a flow rate of 150ml min^{-1} was used for all studies. Sample masses of approximately 1g, of a uniform particle size range of 1.7-2.4mm, were studied using a full scale deflection of 200mg. A movable vertical furnace, was preheated before each experiment and was positioned around the sample after first flushing with high purity argon for 90 min (flow rate 55ml min^{1}) and then flushing with hydrogen for a further 10 min. to establish the reducing atmosphere. At completion of the required reduction period the furnace was lowered and the samples were cooled under argon.

RESULTS AND DISCUSSION

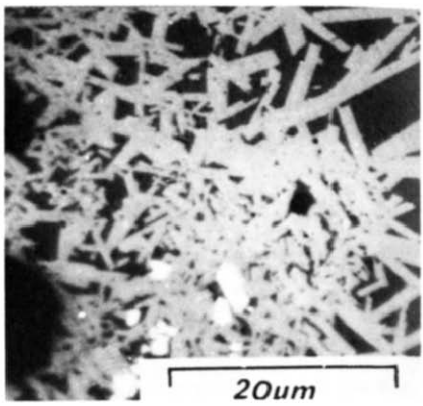
Characterisation of sinters

The sinters were shown to be a complex mixture of phases which varied with the initial coke content. In general the sinters containing the higher levels of carbon were more reduced than those containing the lower levels. Magnetite, the most abundant iron oxide, was present in all the sinters. Hematite was detected in sinters with low coke content whereas wustite was found in the 8% sinter. Iron was also found as calcium ferrite in all the sinters and the most common crystalline silicate was β-dicalcium silicate. The microscopy of the sinters is too complex to be detailed fully in this paper, however, Figures 1(a)-(d) are presented to illustrate some of the various phases. Figure 1(a) shows large euhedral magnetite crystals, formed by primary precipitation from the melt (1-2), which were present as the major iron-bearing phase in all the sinters. Figure 1(b) shows lathes of calcium ferrite which were also found in all the sinters. Figures 1(c) and 1(d) respectively show skeletal and dendritic forms of magnetite and the dendritic form of wustite found in the 8% sinter. The other main microstructural feature of the sinters was porosity which decreased as the carbon content of the sinter mix increased. The porosity indicates the amounts of liquid phase and densification produced in the sinters. A denser sinter may be expected for a higher coke content because either a higher temperature or a longer period at elevated temperature are

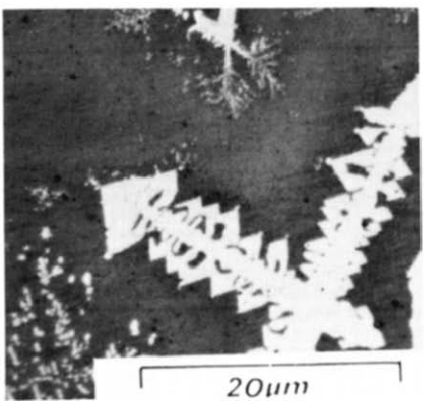
likely as a result of the combustion of the extra coke.



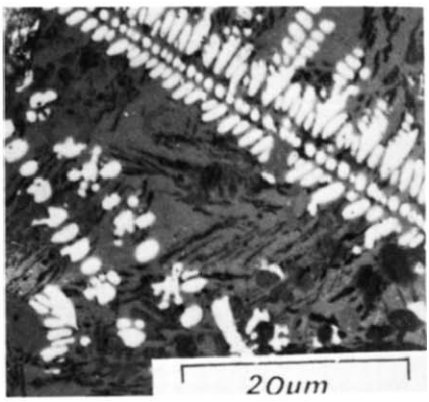
(a)



(b)



(c)



(d)

Figure 1: Optical micrograph of various phases found in the sinters (For description see text).

Reducibility of the sinters

Effect of temperature

The relationship between % weight loss and time at temperatures ranging from 800 to 1100°C are shown in Figures 2 and 3 for the 3.5% and 8% coke sinters. It is evident that the increase in reduction temperature from 1000°C to 1100°C resulted in a decrease in the overall reduction rate whereas increases in temperature from 800°C to 1000°C gave increases in the general reduction rate. This behaviour was observed for all sinters. The decrease in the rate of reduction at 1100°C was not expected as both the kinetics of chemical reaction and the rates of diffusion of reactant and product gases all increase with increase in temperature. For all sinters the initial rate of

reduction is most rapid at 1100°C, however, this changes at approximately 50% of the expected weight loss for full reduction. Microscopical examination of the sinters at this stage shows extensive sintering of the iron product which gives a dense rim around the remaining iron-containing phase. Such sintering has been observed previously in the reduction of iron-bearing materials (3-6). The rim, which impedes access of the hydrogen with the resultant decrease in reduction rate, was particularly evident around the previous euhedral magnetite crystals and the calcium ferrite crystals.

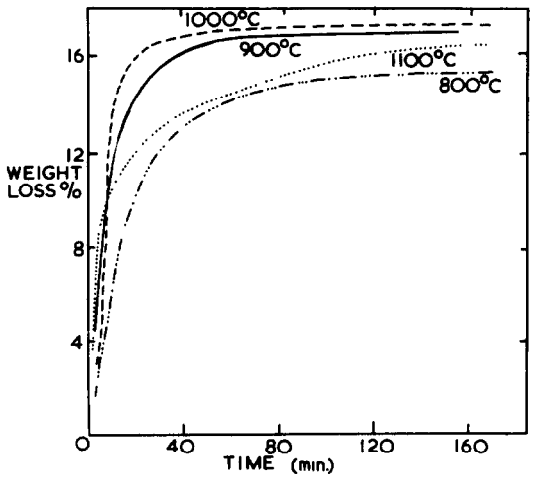


Figure 2: Reduction of 3.5% coke sinter.

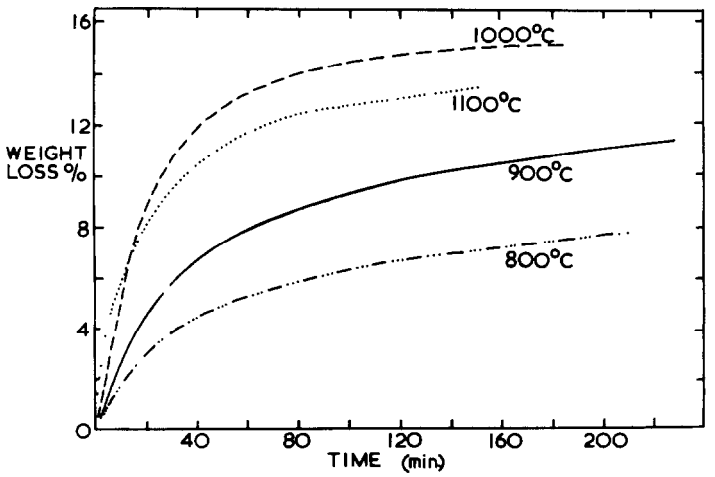
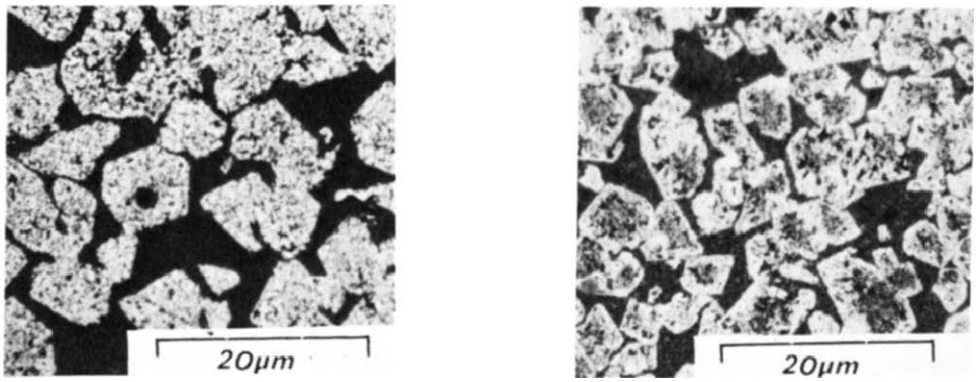


Figure 3: Reduction of 8% coke sinter.

At lower temperatures the iron product remains in the form of separate spherical particles, retained within framework of the original iron-bearing phase, and so offers no extra resistance to the diffusion of hydrogen to the unreduced material. Figures 4(a) and (b) show the products obtained on reduction of the euhedral magnetite at 900°C and 1100°C respectively.



(a) (b)

Figure 4: Products of reduction of euhedral magnetite at (a) 900°C and (b) 1100°C.

Effect of initial coke content

Figure 5 shows a comparison of the reducibilities of all the sinters at 800°C. It is clear that the lower the coke content of the original sinter mix, the higher the reducibility despite the fact that these sinters are in a more oxidised state.

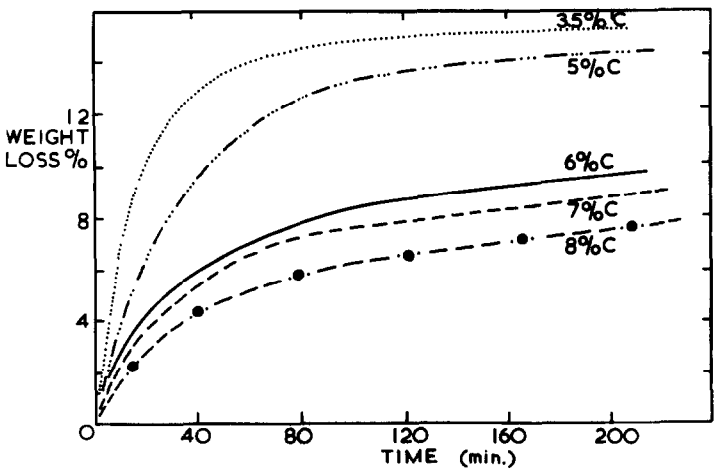


Figure 5: Relationship between weight loss and time for reduction of sinters at 800°C.

The variation in the ultimate weight loss for complete reduction is a result of the different degrees of reduction that occurred during the manufacture of the sinter because of the different coke additions. The difference in reducibility is thus not concerned with the different phases in the sinters (e.g. wustite is found in the 8% sinter, whereas hematite is found in the 3.5% sinter, along with magnetite and calcium ferrite). The important property of the sinters is the porosity which governs the accessibility of the reducing gas to the different phases. Thus the high coke sinters, which are very strong and dense, have low porosity and hence low reducibility.

CONCLUSIONS

(1) The reducibility of a sinter increases with increase in temperature over the range 800-1000°C. However, at 1100°C, although the initial rate of reduction is most rapid, it decreases significantly after approximately 50% reduction as a result of sintering of the iron product.

(2) The reducibility of the sinters is controlled by the porosity which is inversely proportional to the coke addition to the initial sinter mix. Hence low coke sinters have high porosity and high reducibility whereas high coke sinters have low porosity and low reducibility.

REFERENCES

1 N.H. Harbord and D.C. Goldring, J. Iron and Steel Inst., 203 (1965) 349-360.
2 J.T. Fitton and D.C. Goldring, ibid, 204 (1966) 452-458.
3 T.G. Cox and F.R. Sale, Ironmaking and Steelmaking, 1 (1974) 234-238.
4 A.L. Morrison, J.K. Wright and K. McG. Bowling, ibid, 5 (1978) 32-44.
5 H.O. Lien, A. El-Mehairy and H.U. Ross, J. Iron and Steel Inst., 209 (1971) 341-350.
6 F.A. Adedeji and F.R. Sale, Clay Minerals, 19 (1984) 843-856.