JOURNAL OF MATERIALS SCIENCE 10 (1975) 1175–1181

A Mössbauer study of the reduction of hematite in hydrogen at 535° C

M. J. GRAHAM
Division of Chemistry, National Research Council of Canada, Ottawa, K1A 0R9, Ontario, Canada

D. A. CHANNING
Faculty of Technology, The Open University, Milton Keynes, Bucks, UK

G. A. SWALLOW
Materials Division, CEGB, Berkeley Nuclear Laboratories, Berkeley, Glos, UK

R. D. JONES
Department of Metallurgy and Materials Science, University College, Cardiff, UK

The Mössbauer effect has been used to examine the phases produced by hydrogen reduction of hematite to α-iron at 535° C. No evidence has been found for spinels other than that of essentially stoichiometric magnetite; nor has there been any evidence of wüstite formation, in contrast to recent Russian experiments on the reduction of iron oxides at temperatures well below the eutectoid transition point of 570° C.

1. Introduction

We have previously used the Mössbauer effect to study the growth behaviour of oxides formed on α-iron [1-3]. The technique was found to be useful for oxide identification and also for the investigation of growth kinetics. In the present work, we have applied the technique to gain information on the oxides produced during low-temperature hydrogen reduction of hematite (α-Fe_2O_3) to α-iron.

Our interest has been two-fold. First, we aimed to provide information on the form(s) of the spinel phase produced in the reduction process; in particular, whether oxidized or reduced versions of magnetite ($Fe_{3-z}O_4$, $Fe_{3+w}O_4$, respectively) were formed as significant intermediate phases. As far as we are aware, only Colombo *et al.* [4], using chemical, thermogravimetric and X-ray diffraction techniques, have observed a spinel more reduced than magnetite during the gaseous reduction of iron oxides (with w up to 0.06), although Pritchard *et al.* [5] have reported such a phase in a Mössbauer study of the hydrothermal decomposition of $Fe(OH)_2$.

Secondly, we were interested to see whether we could support the recent Mössbauer observations of Romanov *et al.* [6, 7] that wüstite ($Fe_{1-x}O$) is produced during hydrogen reduction of hematite at temperatures substantially below the eutectoid transition point of 570° C.

2. Experimental

The α-Fe_2O_3 starting samples were scales produced by prolonged oxidation of degreased, 9.6 μm thick, iron foils of purity 99.9 + % in 760 Torr oxygen. Reductions were carried out in 1 Torr "static" (i.e. non-flowing) hydrogen; the sample was exposed to the hydrogen before heating to the reduction temperature, and after reduction was quickly cooled to room temperature by removing the furnace and quenching the reaction vessel in cold water. The oxidations and reductions were performed at 535 ± 3° C.

The Mössbauer spectra were recorded in transmission geometry with both source and specimen (the absorber) at room temperature. The spectrometer was of the constant acceleration type employing a 400-channel pulse-height analyser for data storage. As a single-line source, we used 20 mCi of Co^{57} diffused into palladium.

To complement the Mössbauer studies, thermogravimetric measurements were made and some specimen cross-sections examined by optical and scanning electron microscopy.

3. Mössbauer spectra of the iron oxides

Room temperature spectra determined on standard absorbers of wüstite, hematite and the spinels magnetite and maghemite (γ-Fe_2O_3, the equivalent of the oxidized spinel $Fe_{3-z}O_4$ with $z = \frac{1}{3}$) are presented in Fig. 1, together with an α-iron spectrum.

Wüstite shows as a broad paramagnetic singlet. The detailed absorption profile for this oxide depends in a complex way on its defect structure and overall composition [8], frequently appearing as an asymmetric doublet. Like α-Fe, the α-Fe_2O_3 spectrum is a single, six-line, magnetically-split pattern due to Fe nuclei in equivalent environments [9]. In the spinel structure, the cations occupy "A" and "B" sites possessing, respectively, tetrahedral and octahedral symmetries. In stoichiometric magnetite, A sites are occupied by Fe^{3+}, and B sites by equal numbers of Fe^{3+} and Fe^{2+} ions. The Mössbauer absorption of Fe_3O_4 is a superposition of two six-line patterns which are incompletely resolved. The first (with lines labelled A_1, A_2, A_3 . . . in Fig. 1) is due to the Fe^{3+} at A sites, and the second (B_1, B_2, B_3 . . .) is due to the Fe^{2+} and Fe^{3+} at B sites [10]. Fe^{2+} and Fe^{3+} ions at the B sites do not show separate spectra because of the rapid electronic exchange occurring between these ions; the observed spectrum is an average of those expected for the two ion species.

In non-stoichiometric magnetite, $Fe_{3-z}O_4$, it is generally accepted that the cation vacancies occur at the B sites. Charge balance is preserved by a greater proportion of B-site Fe^{3+} ions. According to Daniels and Rosencwaig [11], B-site Fe^{3+} ions which are not paired with Fe^{2+} ions do not take part in fast electronic exchange and give rise to their own six-line pattern which overlaps that due to the A-site Fe^{3+} ions. Thus, compared with stoichiometric magnetite, the effect of an iron deficit is to increase the intensity I_A of the "A pattern" and to decrease the intensity I_B of the "B pattern". The change in intensity ratio I_B/I_A with z is marked, as may be seen directly in the spectra of Coey *et al.* [12]. For example, for $Fe_{2.91}O_4$ they found I_B/I_A =

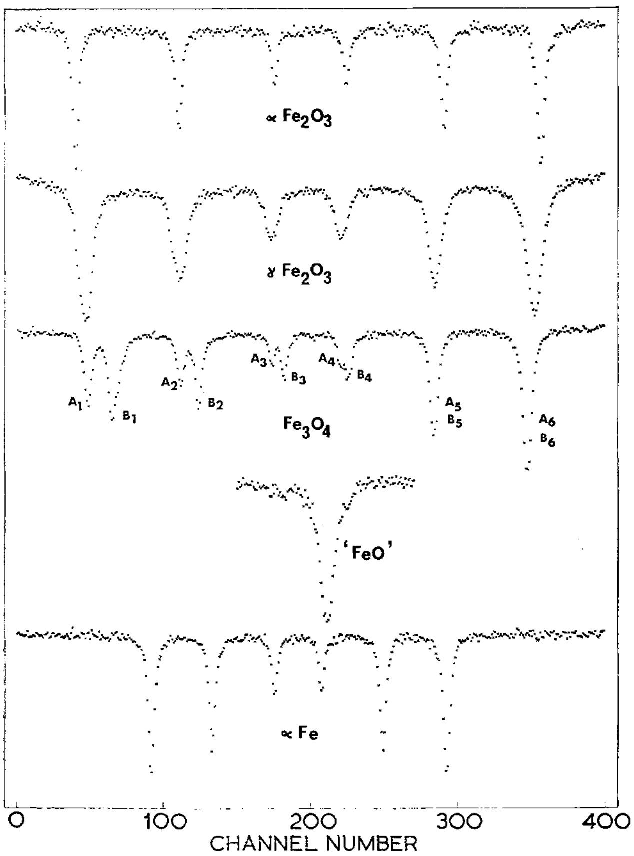

Figure 1 Mössbauer spectra of α-iron, wüstite, magnetite, maghemite and hematite.

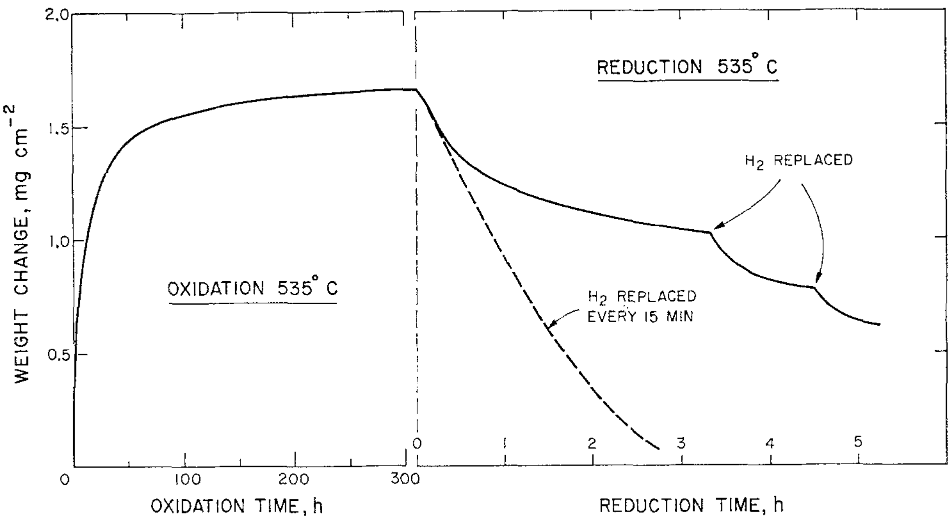

Figure 2 Weight-change curves for complete oxidation of 9.6 μm iron foil at 535°C in 760 Torr oxygen followed by reduction at 535°C in 1 Torr hydrogen.

1.06 which may be compared with $I_B/I_A = 1.88$ expected for Fe_3O_4*. For γ-Fe_2O_3, all cations are Fe^{3+} and the B pattern due to Fe^{2+}/Fe^{3+} pairs is, therefore, of zero intensity; the spectrum is correspondingly a superposition of two unresolved six-line patterns due to Fe^{3+} at the two lattice sites.†

Similar considerations should apply to the reduced form of magnetite, $Fe_{3+w}O_4$, reported by Colombo *et al.* [4] and Pritchard *et al.* [5]. In this case, however, there will be an excess of Fe^{2+} (relative to Fe_3O_4) in octahedral sites. From the work of Pritchard *et al.* [5] we can expect that Fe^{2+} not paired with B-site Fe^{3+} ions will produce a six-line pattern with splitting ~ 7% less than the Fe^{2+}/Fe^{3+} B pattern. Consequently, it should be readily distinguishable from the normal A and B spectra. The appearance of this third six-line spectrum in $Fe_{3+w}O_4$ should also be accompanied by a decrease in the intensity of the B pattern (as for $Fe_{3-z}O_4$) due to a reduced number of B-site Fe^{2+}/Fe^{3+} pairs.

4. Results and discussion

4.1. General

As may be noted in the thermogravimetric data of Fig. 2, in preparing the starting hematite it was necessary to oxidize the iron foils for ~ 300 h at 535°C for complete conversion of metal to the oxide. The cross-sections in Fig. 3 show that a fairly uniform layer of oxide was produced and provide information on the α-Fe_2O_3

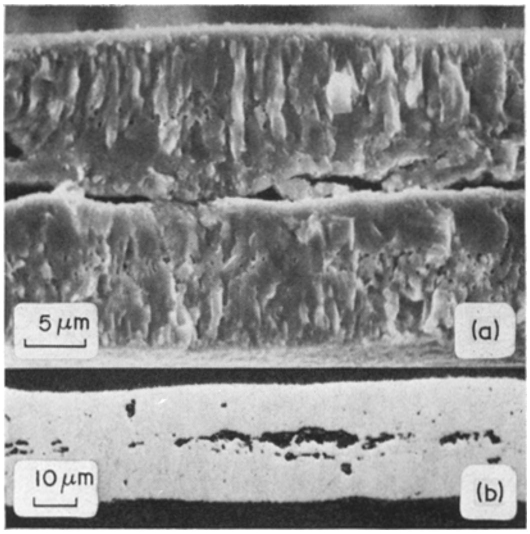

Figure 3 Sections through hematite produced from 9.6 μm iron foil heated at 535°C in 760 Torr oxygen for ~ 300 h. (a) scanning electron micrograph of fracture section; (b) metallographic cross-section.

---

*I_B/I_A is not equal to 2, as would be expected from the site occupancy in stoichiometric magnetite, because the recoil-free fractions differ slightly for the two Fe sites [13]. The expected value of 1.88 also assumes that thin absorbers are used. In practice, observed values of I_B/I_A are likely to extend down to around 1.80 because of thickness effects.

†The line-widths in our γ-Fe_2O_3 standard spectrum appear to be greater than those in the γ-Fe_2O_3 spectrum of Coey *et al.* [12]. Possibly this is an impurity effect.

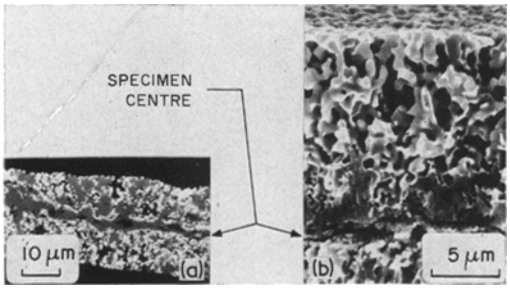

Figure 4 Sections through specimen reduced at 535°C for 3 h, H_2 replaced every 15 min: (a) metallographic cross-section showing the distribution of α-Fe (white phase) in spinel (grey phase); (b) scanning electron micrograph of fracture section shows α-Fe to be porous.

grain structure. The scale (Fig. 3a) is seen to be mainly columnar with a finer-grained outer layer and a coarser-grained oxide towards the centre.

The weight-loss curves of Fig. 2 illustrate the overall reduction behaviour of our hematite scales. The upper curve indicates that the reduction rate in static hydrogen was initially rapid, but slowed considerably with time. The latter can be attributed to a lowering of the reducing capability of the gas as the H_2O/H_2 ratio increased. By replacing the reducing gas with fresh hydrogen, a fast reduction rate could be re-established, as shown at 3.3 h and 4.5 h.The lower curve in Fig. 2 was obtained by replacing the reducing gas with fresh hydrogen every 15 min. The curve is smooth and the reduction remained at a fast rate. Reduction procedures with or without fresh hydrogen replacement were used to produce specimens at various stages of conversion of α-Fe_2O_3 back to α-Fe for the Mössbauer analysis. The weight-loss curves presented are meant to show fairly typical behaviour; however, it must be noted that, for a given reduction schedule, the extent of reduction between specimens was found to vary considerably (e.g. by a factor of 2 in oxygen loss). This is not surprising perhaps in view of the generally complex structure of the reduced scales revealed in cross-sections. For example, Fig. 4 shows sections of a specimen reduced to ~ 50% metal. It is evident that α-iron is scattered throughout the spinel oxide (Fig. 4a) rather than continuing to grow as an outer layer; extensive hydrogen transport has occurred down cracks/pores in the oxide and the highly porous metal (Fig. 4b) has permitted continued ingress of hydrogen for further reduction.

Some representative Mössbauer spectra of reduced hematite scales are shown in Fig. 5. Also included is spectrum (a) for unreduced oxide. Spectrum (b) is for a scale reduced for 5 min. Some spinel has been produced, but α-Fe_2O_3 remains the major phase. After a 10 min reduction, spectrum (c), further development of the spinel is apparent. The relative total absorption intensities due to spinel and α-Fe_2O_3 show that the sample consisted very roughly of equal proportions of the two components. Spectrum (d), obtained following a 3.3 h reduction (without hydrogen replacement, as for (b) and (c)) shows spinel as the major phase, although a substantial amount of α-Fe_2O_3 is still evident. Spectra (e) and (f) are for oxides more extensively reduced and in both cases the α-Fe_2O_3 has been totally reduced to spinel and metal. Spectrum (e) was observed for the specimen used in determining the upper reduction curve of Fig. 2, and thus corresponded to a 5.2 h reduction with two hydrogen replacements, while (f) was obtained by reducing for a period of 3 h with hydrogen replacement at 15 min intervals.

In the spectra presented in Fig. 5, and indeed in all our reduction experiments at 535°C, we have found no evidence of wüstite formation. This is, of course, consistent with the iron-oxygen phase diagram, but contrasts with the Russian Mössbauer data [6, 7] which indicate that wüstite forms on reduction of iron oxides at temperatures as low as 425°C. By reducing our hematite scales at temperatures greater than 570°C, we had no difficulty in producing wüstite. In Fig. 6, for example, we show the spectrum of an α-Fe_2O_3 specimen reduced at 595°C. The reduction time was 20 min, with hydrogen replacement at the 10 min mark. In addition to α-Fe and spinel, wüstite is strikingly evident as the intense central absorption. (This observation of wüstite provided a check that our quenching procedure to room temperature was sufficiently rapid to retain the oxide as a metastable phase.)

4.2. Reduction of α-Fe_2O_3 to spinel

The initial reduction at 535°C of α-Fe_2O_3 to spinel was observed to be a fairly rapid process. It was also evident from Mössbauer spectroscopy and metallography that α-Fe did not form in significant quantities until the hematite had completely converted to the spinel phase.

Two possible mechanisms for the low-temperature reduction of α-Fe_2O_3 to spinel were

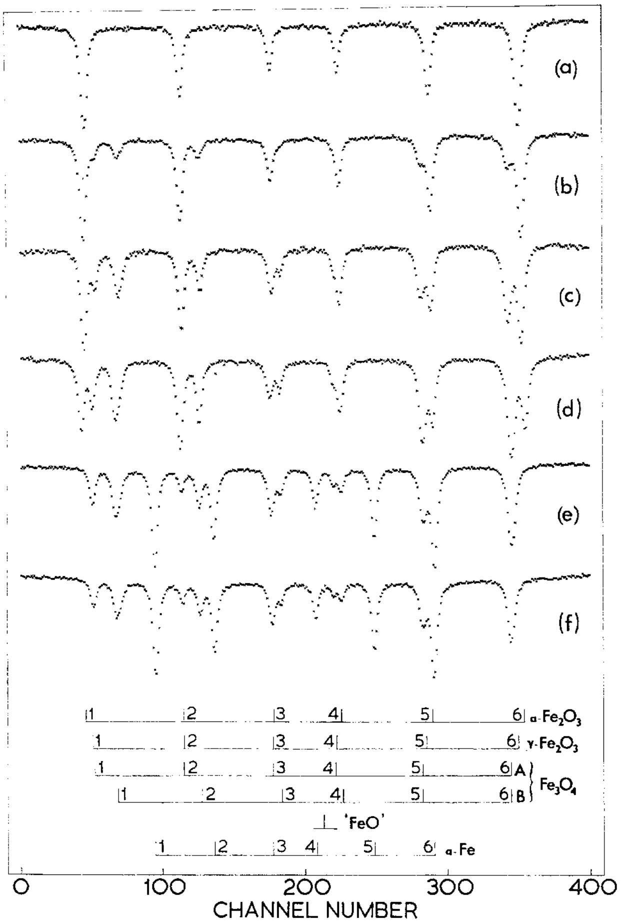

Figure 5 Mössbauer spectra of α-Fe_2O_3 reduced in H_2 at 535°C for the following times: (a) 0 min; (b) 5 min; (c) 10 min; (d) 3.3 h; (e) 5.2 h, H_2 replaced twice (specimen used for upper reduction curve of Fig. 2); (f) 3 h, H_2 replaced every 15 min.

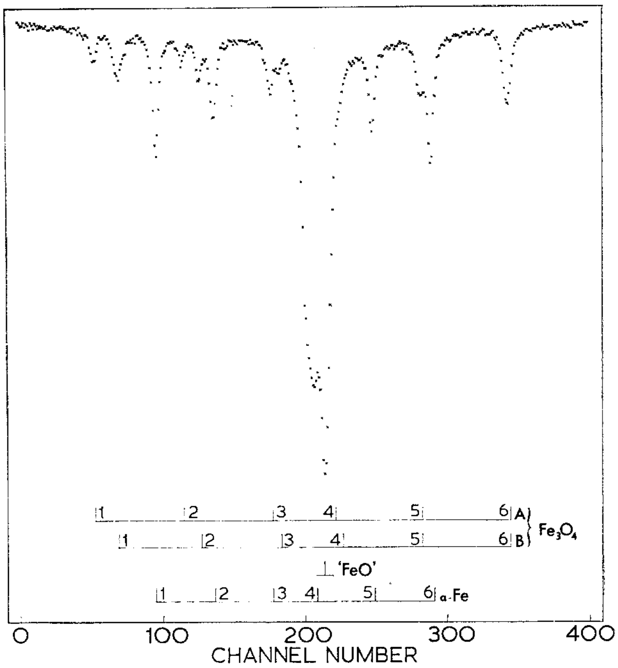

Figure 6 Mössbauer spectrum of α-Fe_2O_3 reduced in H_2 at 595°C for 20 min with H_2 replaced after 10 min. Note the strong central absorption due to wüstite.

outlined by Colombo *et al.* [4]. The first, which their experiments support, postulates the direct conversion of hematite to stoichiometric magnetite, while in the second it is proposed that α-Fe_2O_3 converts first into a spinel more oxidized than Fe_3O_4, i.e. γ-Fe_2O_3 or $Fe_{3-z}O_4$. It is immediately evident from spectra (b), (c) and (d) of Fig. 5, which show only α-Fe_2O_3 and spinel, that the spinel composition does not correspond to γ-Fe_2O_3. It is also evident from Section 3 that the overall composition of the spinel does not correspond to a highly oxidized form of magnetite, since the intensity ratio I_B/I_A associated with the spinel A and B subpatterns is substantially greater than unity. This is readily seen by comparing the intensities I_{A_1} and I_{B_1} of the first lines A_1 and B_1 of the subpatterns and by appreciating that I_{B_1}/I_{A_1} may be equated with I_B/I_A. Evaluation of I_{A_1} and I_{B_1} in spectra (b), (c) and (d), by both computer and hand-fitting procedures, yielded ratios I_B/I_A as follows: spectrum (b), 1.83 ± 0.15; spectrum (c), 1.76 ± 0.15; and spectrum (d), 1.91 ± 0.15. Comparing these ratios with the thin-absorber value of 1.88 characteristic of Fe_3O_4, it may be concluded that the spinel formed during this stage of reduction is essentially of stoichiometric magnetite. If an intermediate, highly oxidized magnetite did form in our experiments, it clearly represented only a small proportion of the spinel phase.

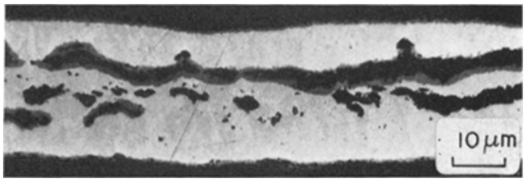

Figure 7 Metallographic cross-section of α-Fe_2O_3 at an early stage of reduction in H_2 at 535°C. Note the thin external magnetite layer, and also the lining of magnetite within cavities which are presumably open to the reducing gas.

Assuming that α-Fe_2O_3 does convert directly to Fe_3O_4, hydrogen reacts with the surface oxygen of the hematite to produce water vapour and, after a short time, a surface layer of magnetite (cf. Fig. 7). As detailed by Colombo *et al.* [4], this removal of oxygen is accompanied by the reduction of ferric to ferrous ions which provoke local rearrangement of the lattice to form the spinel phase. In continued reduction, Fe^{2+} ions diffuse through the magnetite and convert hematite to magnetite at the spinel/hematite interface. This migration of Fe^{2+} ions probably occurs via easy diffusion paths (e.g. grain boundaries) and the process continues until all the α-Fe_2O_3 has been transformed to Fe_3O_4.

4.3. Reduction of Fe_3O_4 to α-Fe

Following complete conversion of their powdered α-Fe_2O_3 to Fe_3O_4, Colombo *et al.* [4] observed an induction period during which the reduced version of magnetite, $Fe_{3+w}O_4$, was formed together with a small quantity of α-Fe. At the end of the induction period, the reduced spinel proceeded to convert to α-Fe. Their overall scheme could be summarized as follows:

$$\alpha\text{-}Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_{3+w}O_4 + \alpha\text{-}Fe \rightarrow \alpha\text{-}Fe\,.$$

In Section 3, it was seen that the spinel $Fe_{3+w}O_4$ should give rise to a Mössbauer spectrum consisting of three partially resolved six-line patterns: the normal A and B patterns plus a further pattern, of smaller splitting, due to non-paired Fe^{2+} ions at the octahedral sites. Inspection of the spectra (e) and (f) in Fig. 5, where spinel and α-Fe are the only phases indicated, reveals no evidence of a third pattern due to non-paired, Fe^{2+} ions. To indicate the sensitivity of the Mössbauer technique for observing a reduced spinel, via this third pattern, it may be noted that for a sample with a 1% iron excess ($Fe_{3.03}O_4$) 5% of the cations in the oxide will be non-paired Fe^{2+} octahedral ions, if we accept the proposition [4, 5] that the tetrahedral sites are filled as in stoichiometric magnetite.* The corresponding level of resonant absorption, ~ 5% of the spinel total, would be just within the anticipated detection limit.

Analysis for I_B/I_A of the spinel component in spectra (e) and (f) gave the values 1.74 ± 0.15 and 1.77 ± 0.15 respectively which are essentially as found earlier in spectra (b), (c) and (d). It is apparent that the overall composition of the spinel produced is again virtually that of stoichiometric magnetite.

5. Conclusion

Mössbauer spectroscopy has shown that in H_2 at 535°C α-Fe_2O_3 is reduced to α-iron through

---

*If the tetrahedral sites are occupied as in stoichiometric magnetite, then, per formula unit, the occupancy of the octahedral sites will be $1 + 3w$ Fe^{2+} and $1 - 2w$ Fe^{3+}. The corresponding number of non-paired Fe^{2+} ions is $5w$.

essentially stoichiometric magnetite. No evidence has been found for γ-Fe_2O_3, oxidized or reduced forms of magnetite as significant intermediate phases. Nor has there been any indication of wüstite formation at this temperature, in contrast to Russian Mössbauer observations that wüstite is produced by reduction of iron oxides at temperatures well below 570°C.

Acknowledgements

The authors thank Dr R. J. Hussey for the weight-change measurements, and P. E. Beaubien and G. I. Sproule for skilful assistance in examining specimen cross-sections. Part of this work was completed at Berkeley Nuclear Laboratories; permission to publish the paper has been given by the Central Electricity Generating Board.

References

1. D. A. CHANNING and M. J. GRAHAM, CEGB Report No. RD/B/N1384 (1969).
2. *Idem*, *Corrosion Sci.* **12** (1972) 271.
3. D. A. CHANNING, M. J. GRAHAM and S. M. DICKERSON, *ibid* **13** (1973) 933.
4. U. COLOMBO, F. GAZZARRINI and G. LANZAVECCHIA, *Mater. Sci. Eng.* **2** (1967) 125.
5. A. M. PRITCHARD, J. R. HADDON and G. N. WALTON, *Corrosion Sci.* **11** (1971) 11.
6. V. P. ROMANOV, P. A. TATSIENKO, L. F. CHECHERSKAYA, G. P. BASANTSEV and V. D. CHECHERSKII, *Inorg. Mat.* (*USSR*) English Translation **7** (1971) 396.
7. V. P. ROMANOV, L. F. CHECHERSKAYA and P. A. TATSIENKO, *Phys. Stat. Sol.* (*a*) **15** (1973) 721.
8. N. N. GREENWOOD and A. T. HOWE, *J. Chem. Soc. Dalton Trans.* **1** (1972) 110.
9. O. C. KISTNER and A. W. SUNYAR, *Phys. Rev. Letters* **4** (1960) 412.
10. R. BAUMINGER, S. G. COHEN, A. MARINOV, S. OFER and E. SEGAL, *Phys. Rev.* **122** (1961) 1447.
11. J. M. DANIELS and A. ROSENCWAIG, *J. Phys. Chem. Sol.* **30** (1969) 1561.
12. J. M. D. COEY, A. H. MORRISH and G. A. SAWATZKY, *J. de Physique, Colloque C1*, Supplément No. 2-3, **32** (1971) C1-271.
13. G. A. SAWATZKY, F. VAN DER WOUDE and A. H. MORRISH, *Phys. Rev.* **183** (1969) 383.

Received 29 November and accepted 18 December 1974.