JOURNAL OF MATERIALS SCIENCE 22 (1987) 438–442

Formation and stability of γ-iron in high-temperature treated nontronite

JACQUES VAN WONTERGHEM, STEEN MØRUP
Laboratory of Applied Physics II, Technical University of Denmark, DK-2800 Lyngby, Denmark
JØRGEN VILLADSEN
Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark
CHRISTIAN J. W. KOCH*
Chemistry Department, Royal Veterinary and Agricultural University, DK-1871 Frederiksberg C, Denmark

Samples of nontronite, exposed to different high-temperature treatments, have been studied by Mössbauer spectroscopy and X-ray diffractometry. Oxidation and subsequent reduction at 900 to 1000° C resulted in formation of metallic iron with about 20 at % of the total iron content as the γ-phase of iron. Investigations of the phases formed during the oxidation and reduction steps and studies of the stability of the γ-iron suggests that the γ-iron formed by this method is stabilized by impurities

1. Introduction

In two previous papers [1, 2] MacKenzie and Bowden described an unusual singlet peak in Mössbauer spectra of various iron–silicate systems, which had been oxidized in air at 1300° C and subsequently reduced in a mixture of 5% H_2 and 95% N_2. It was proposed that the singlet peak was either due to Fe(II) in the low-spin state or due to superparamagnetic α-iron particles.

In a later paper [3] we have shown that the singlet peak in the Mössbauer spectrum is due to γ-iron. In this study samples were produced by oxidation of nontronite (an iron-containing layer silicate) at about 1000° C, followed by reduction in pure hydrogen gas at the same temperature. Approximately 20 at % of the iron was found to be present as γ-iron. Since pure γ-iron is only stable at temperatures above 910° C, further investigations have been carried out in order to elucidate the mechanism of formation and to study the stability of the γ-iron produced by high-temperature treatments of nontronite.

2. Experimental procedure

The samples investigated were powdered nontronites from Garfield and Manito, Washington (reference clay mineral Nos H-33a and H-33b, respectively [4]). Heat treatments, i.e. oxidations or reductions, were carried out in a quartz furnace with the facility of controlled gas-flow (air or hydrogen). For *in situ* measurements a quartz *in situ* cell, similar to the pyrex cell described earlier [5], was used.

Mössbauer absorbers were prepared from the powdered samples which were pressed in plexiglass absorber holders. Absorbers used in the *in situ* study were prepared by pressing a pellet of the powdered nontronite. The sample thickness was about 40 mg powder per cm^2. The spectra were obtained using conventional constant-acceleration Mössbauer spectrometers with sources of ^{57}Co in rhodium. The spectrometer was calibrated by use of a 12.5 μm absorber foil of α-iron at room temperature. Isomer shifts are given relative to the centroid of the spectrum of this α-iron absorber. Computer analysis of the Mössbauer spectra was carried out using a least-squares fitting programme.

X-ray diffraction (XRD) patterns were recorded using conventional vertical diffractometers equipped with a diffracted-beam graphite monochromator. The $K\alpha$ doublets from copper and cobalt tubes were used as X-ray radiation.

3. Results

3.1. Oxidation products

In previous studies it was shown that the singlet line in the Mössbauer spectra could only be observed if the iron–silicate systems had been oxidized at a high temperature before the reduction [1, 2]. Similar observations have been made in the present studies of nontronite. The oxidation has to take place at temperatures above approximately 600° C, i.e. at temperatures at which breakdown of the layer silicate structure occurs [6].

Fig. 1 shows Mössbauer spectra of two different samples of nontronite, oxidized in air at 952° C for 2 h and measured at 295 and 80 K. From the figure it is seen that the Mössbauer spectra consist of several six-line components.

The room temperature parameters of the spectra in Fig. 1 are given in Table I. The presence of (at least) three different magnetically split components in the

---

* *Present address*: Geological Survey of Denmark, Thoravej 31, DK-2400 Copenhagen NV, Denmark.

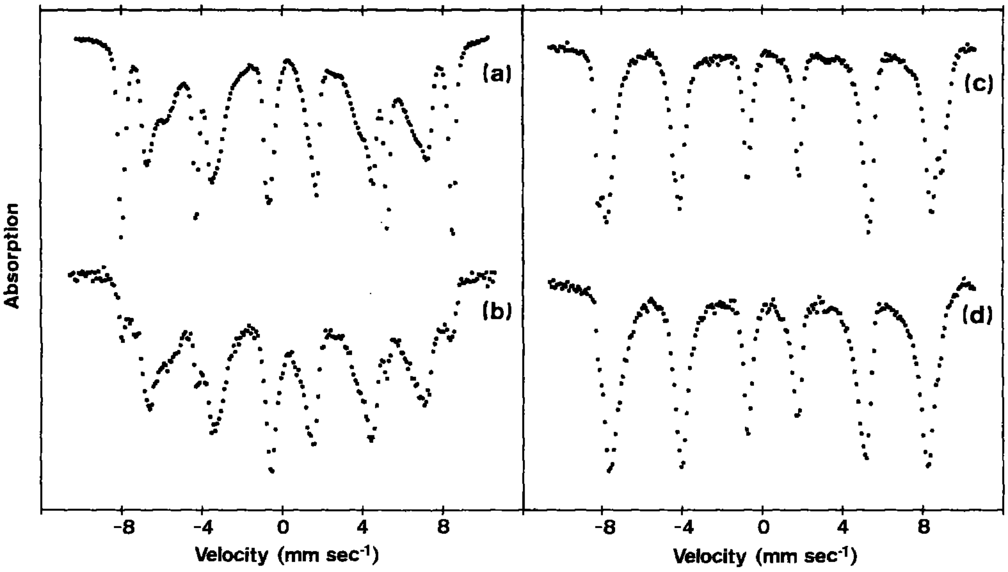

Figure 1 Mössbauer spectra of the nontronites, oxidized at 952° C for 1 h. (a) H-33a (Garfield) at 295 K; (b) H-33b (Manito) at 295 K; (c) H-33a at 80 K; (d) H-33b at 80 K.

spectra and the fact that the magnetic hyperfine fields exhibit different temperature dependences suggest that iron is present in at least three different phases. One of them (Component A) has Mössbauer parameters close to those of haematite, but the magnetic hyperfine field is slightly smaller than that of pure haematite. This suggests that some impurities are substituted into the lattice.

The Mössbauer parameters of Component B suggest that it is due to a mixed oxide phase, and the parameters of Component C are in good agreement with those of ε-Fe_2O_3 obtained by Dezsi and Coey [7]. This assignment is supported by the XRD studies of the samples which showed diffraction lines indicating the presence of haematite, ε-Fe_2O_3 [8], cristobalite and possibly also a mixed oxide phase. Components B and C exhibit very broad Mössbauer lines suggesting that they contain impurity atoms or that they are poorly crystallized. The presence of impurities in haematite and ε-Fe_2O_3 was also suggested by small displacements of the diffraction lines. Thus, the study of the oxidized samples revealed that several iron oxide phases are formed during the oxidation step and that they contain impurities.

3.2. Reduction products

The singlet line in the room-temperature Mössbauer spectra of the samples, reduced at about 1000° C, has a line width of 0.29 mm sec^{-1}, an isomer shift of -0.09 mm sec^{-1} and a relative area of about 20%. At 4.2 K the line width of the singlet line increases to about 1.0 mm sec^{-1} [3].

A computer fit of the same component at 4.2 K with a six-line Zeeman pattern yielded a magnetic hyperfine field of about 2.6 T [3]. Earlier studies have shown that the Mössbauer spectra of γ-iron at room temperature consists of a single line with isomer shift of about -0.088 mm sec^{-1} and a line width of about 0.3 mm sec^{-1} [9]. The γ-iron phase becomes antiferromagnetic below about 80 K with a magnetic hyperfine field of about 2.4 T at 4.2 K [9].

XRD studies on the present reduced samples revealed the presence of α-quartz, cristobalite, α-iron and γ-iron. The lattice constant for the γ-iron was measured to $a = 0.3583$ nm in good agreement with, but slightly smaller than, the value obtained by Newkirk [10]. From the broadening of the diffraction lines a particle size of 110 nm was estimated.

Thus the singlet line found in the Mössbauer spectra of the reduced samples can unambiguously be identified as being due to γ-iron.

In order to investigate the influence of the reduction temperature on the relative amounts of the different components in the sample, we have obtained Mössbauer spectra of samples of the nontronite H-33b. The nontronite was oxidized at 952° C for 1 h and samples were subsequently reduced at different temperatures for 2 h. The results of reducing at 524, 612, 704, 800, 880 and 952° C are illustrated in the room temperature Mössbauer spectra shown in Fig. 2.

TABLE I Magnetic hyperfine field, B, quadrupole shift, ε, isomer shift, δ_{Fe}, line width, Γ, and relative area, A_{rel}, of the components present in the room-temperature Mössbauer spectra of the samples of oxidized nontronite

Sample	Component	B(T)	ε(mm sec^{-1})	δ_{Fe} (mm sec^{-1})	Γ (mm sec^{-1})	A_{rel} (%)
H33-a	A	51.2 ± 0.2	−0.11 ± 0.02	0.38 ± 0.02	0.34 ± 0.06	25 ± 3
	B	43.0 ± 0.4	−0.14 ± 0.04	0.38 ± 0.04	0.70 ± 0.12	25 ± 3
	C	37.6 ± 0.4	−0.05 ± 0.07	0.36 ± 0.07	1.20 ± 0.19	50 ± 5
H33-b	A	50.8 ± 0.6	−0.12 ± 0.10	0.37 ± 0.10	0.48 ± 0.20	13 ± 5
	B	42.8 ± 0.3	−0.12 ± 0.05	0.37 ± 0.05	1.02 ± 0.14	30 ± 3
	C.	36.8 ± 0.3	−0.02 ± 0.02	0.39 ± 0.02	1.40 ± 0.26	57 ± 6

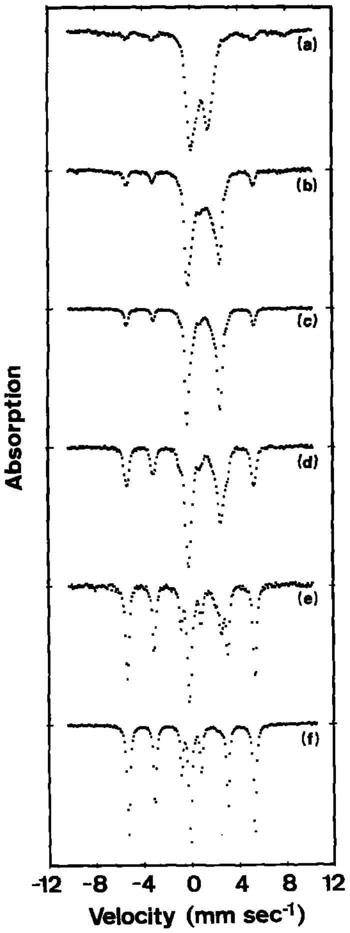

Figure 2 Room-temperature Mössbauer spectra of nontronite (H-33b), oxidized at 952° C for 1 h and reduced in pure hydrogen for 2 h at: (a) 524° C; (b) 612° C; (c) 704° C; (d) 800° C; (e) 880° C; (f) 952° C.

It is seen that α-iron is formed at temperatures above approximately 500° C, whereas γ-iron is formed above approximately 700° C. Above these minimum reduction temperatures the yield of α- and γ-iron increases with increasing temperature.

At the lower reduction temperatures there is a remanence of Fe^{3+}-containing oxide phases. Low-temperature spectra indicate that they exhibit superparamagnetic relaxation. Furthermore, it is seen that more than half of the iron is present as Fe^{2+} between 400 and 800° C. XRD studies showed the presence of an iron-rich olivine in these samples.

Assuming identical f-factors of the components, we have calculated the distribution between γ-iron, α-iron, Fe^{3+} and Fe^{2+} in the samples as a function of the reduction temperature (Fig. 3). It is noticeable that γ-iron is formed at a temperature far below the α- to γ-iron transition temperature (910° C for pure iron). This suggests that the γ-iron does not form via an α- to γ-iron transition, and it is therefore likely that the formation of γ-iron is related to a structural stabilization by impurity atoms.

3.3. Cooling rate dependence

In order to examine the influence of the cooling rate on the amount of γ-iron in the reduced samples, we have compared two samples prepared from nontronite H33-b. Both samples were preoxidized at 952° C for 1 h and reduced in pure H_2 at 952° C for 1 h. One sample was cooled to room temperature in about 0.5 h, which is the cooling time normally used during these investigations. The other sample was cooled slowly over a period of about 10 h. Mössbauer spectra of the two samples were obtained at room temperature and the corresponding computer fits of the spectra revealed that there were no significant differences in the distribution of components in the two samples, i.e. about 18 at % γ-iron, 78 at % α-iron and 4 at % Fe^{2+}. This finding indicates that the presence of γ-iron in the samples is not due to quenching.

3.4. Stability of the γ-iron during high-temperature treatment

It is commonly found that γ-iron produced by quenching of steel can be annealed into α-iron by heating at about 200° C (see e.g. [11]).

To investigate the stability of the γ-iron formed by oxidation and reduction of the nontronite at 952° C,

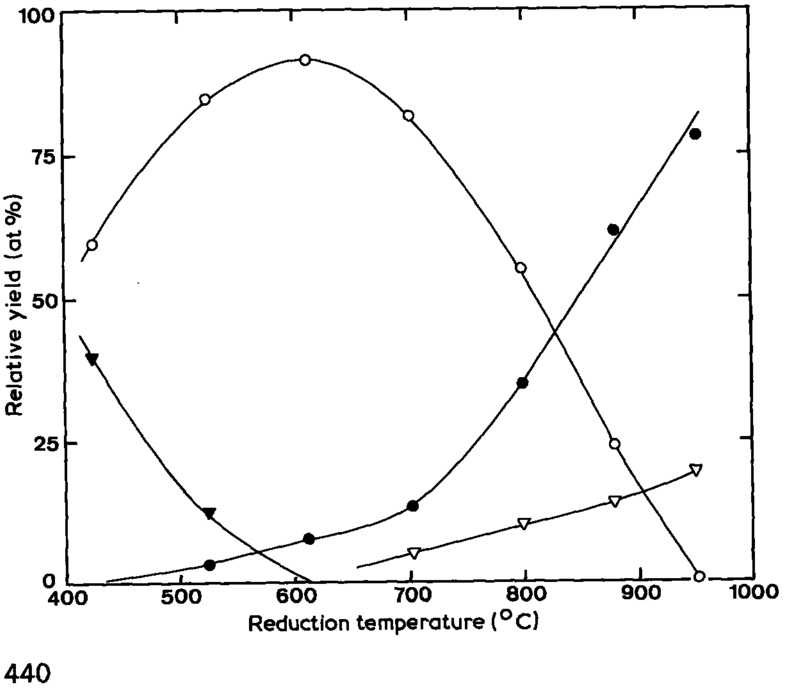

Figure 3 Relative amounts of (○) Fe^{2+}, (▼) Fe^{3+}, (●) α-iron and (▽) γ-iron as a function of reduction temperature as calculated from the Mössbauer spectra.

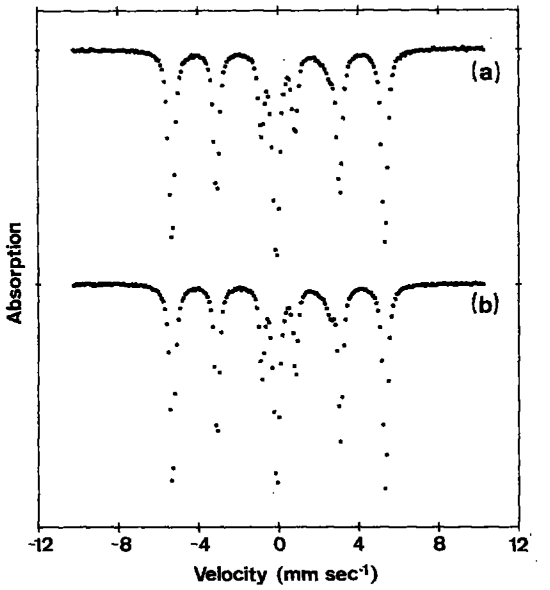

Figure 4 Room-temperature Mössbauer spectra of a sample containing about 20 at % γ-iron, which has been heated in pure hydrogen for 4 h at: (a) 196° C; (b) 704° C.

we have heated samples containing about 20 at % γ-iron in pure hydrogen at temperatures of 196, 310, 422, 524, 612 and 704° C for 4 h, after which room-temperature Mössbauer spectra of the different samples were obtained. The spectra obtained after heating at 196 and 704° C are shown in Fig. 4. The Mössbauer spectra revealed no significant differences in the relative amounts of γ-iron, α-iron and Fe^{2+}. Heating at the intermediate temperatures resulted in similar spectra. These results show that it is not possible to induce a conversion of the γ-iron phase into α-iron by heating at temperatures up to 704° C. Furthermore, it was found that even after heating at 310° C for 28 h there were no significant changes in the relative distribution of the components.

Thus the γ-iron produced by the present method seems to be rather stable when heated in hydrogen. The possibility that hydrogen itself could be a stabilizing element was investigated by heating a sample in ultra-high vacuum at 400° C for 4 h. This treatment caused no change in the relative amount of γ-iron. Therefore other impurities must be responsible for the stability of the γ-iron.

3.5. *In situ* measurements

In an attempt to study the formation of the γ-iron, e.g. determine the formation temperature, we have studied the reduction *in situ* at temperatures of up to about 900° C. This was carried out as follows: a pellet of preoxidized nontronite (952° C, 1 h) was placed in the *in situ* quartz cell and reduced in an H_2 flow for 24 h at a given temperature, after which a Mössbauer spectrum was recorded at the same temperature. The temperature was then raised and the sample was again reduced for 24 h followed by the recording of a Mössbauer spectrum – and so on. Fig. 5 shows the result of these *in situ* Mössbauer measurements made at temperatures of 540, 630, 700 and 800° C.

With increasing temperature we observe a decrease in the relative amounts of Fe^{2+} and Fe^{3+} and an

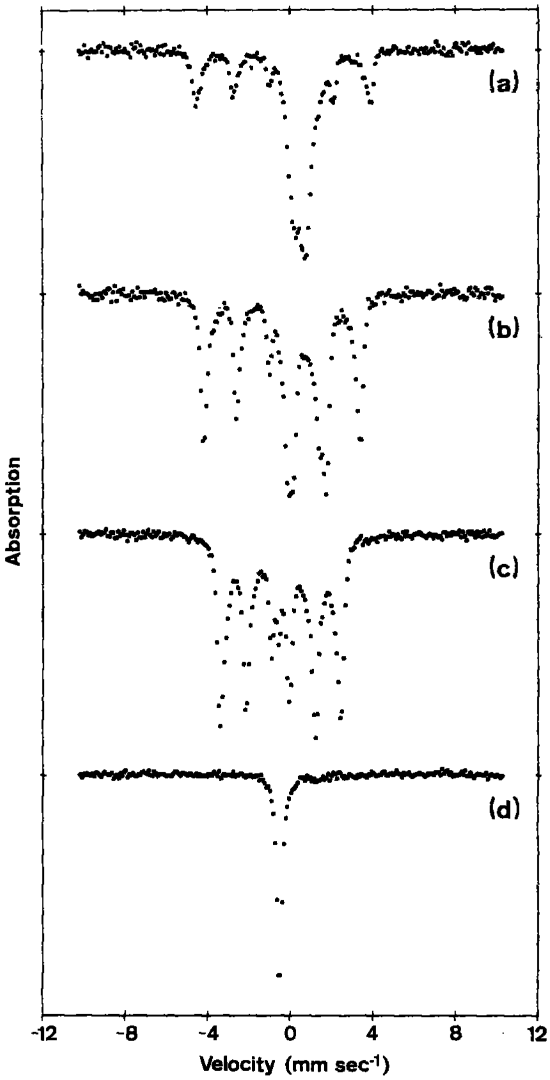

Figure 5 In situ Mössbauer spectra of preoxidized nontronite in H_2. The spectra were obtained at (a) 540° C; (b) 630° C; (c) 700° C; (d) 800° C.

increase in the relative amounts of γ-iron and α-iron. Furthermore, a gradual collapse of the magnetic hyperfine splitting in the α-iron is observed as the temperature approaches the Curie temperature (T_c = 773° C). The amount of γ-iron, estimated from the high-temperature spectra, does not significantly differ from those estimated from the spectra obtained at room temperature (Figs 2 and 3).

3.6. Reduction of sintered oxide

From a chemical analysis of the nontronites, one can propose four major elements being the most probable stabilizing impurity atoms in the γ-iron, i.e. silicon, aluminium, magnesium and calcium, arranged according to the amount in which they occur in the clay mineral [4]. We have therefore carried out experiments in which haematite and oxides of these elements have been sintered together in air at about 1000° C, and subsequently reduced in pure hydrogen at the same temperature. Only in the case of calcium was it found possible to produce γ-iron. This result suggests that calcium atoms might be involved in the stabilization of the γ-iron. MacKenzie and Bowden [2] also produced γ-iron from sintered oxides of calcium and iron.

4. Discussion

The results of the room-temperature study of the reduced samples showed a minimum reduction temperature of approximately 600° C for the formation of γ-iron, i.e. at a temperature below the α- to γ-iron transition. This finding suggests that the γ- and α-iron form independently. The finding that it is possible to produce γ-iron by reduction of a sintered mixture of iron and calcium oxides suggests that the presence of metal ions other than iron in the phases formed during the oxidation step is essential for the formation of γ-iron. As all the phases formed from oxidation of nontronite show evidence of substitution it is not possible to identify a specific phase as the precursor for γ-iron. The necessity for the mixing of impurities into an iron oxide phase prior to reduction also explain the finding that γ-iron cannot be produced by a direct reduction of nontronite.

The way in which impurity atoms stabilize the γ-iron is of great interest. One possibility is that the impurity atoms simply substitute for iron atoms in the lattice. The atomic radius of calcium atoms (0.197 nm) is, however, much larger than that of iron atoms (0.126 nm) [12], and therefore such a substitution is in general not likely. In fact the solubility of calcium in α-iron is extremely small [13]. One possible explanation of the results could be that calcium is soluble in γ-iron at high temperatures. The stability of the phase may then be related to the fact that calcium is insoluble in α-iron, i.e. the γ-phase is prevented from transforming to the α-phase because the calcium cannot be accommodated in the α-phase. It is, however, also possible that the small size of the γ-iron particles may have an influence on the γ → α transition temperature [14].

5. Conclusion

The present studies have shown that γ-iron can be formed by reduction of high-temperature oxidized nontronite, and that this γ-iron does not transform into α-iron during heating. The formation of γ-iron in this system probably depends on the presence of impurities in the precursor phase(s).

Acknowledgements

Support from the Danish Technical Research Council is gratefully acknowledged. The authors are grateful to V. F. Buchwald for valuable discussions.

References

1. K. J. D. MacKENZIE, *J. Mater. Sci.* **17** (1982) 1834.
2. K. J. D. MacKENZIE and M. E. BOWDEN, *J. Mater. Sci. Lett.* **2** (1983) 317.
3. J. VAN WONTERGHEM, S. MØRUP and C. J. W. KOCH, *ibid.* **3** (1984) 1080.
4. P. F. KERR, "Reference Clay Minerals", American Petroleum Institute Research Project 49 (Columbia University, New York, 1951).
5. H. TOPSØE, B. S. CLAUSEN, R. CANDIA, C. WIVEL and S. MØRUP, *J. Catal.* **68** (1981) 433.
6. R. W. GRIMSHAW, "The Chemistry and Physics of Clay and Allied Ceramic Matrials", 4th Edn (Ernest Benn, London, 1971) pp. 698–772.
7. I. DEZSI and J. M. D. COEY, *Phys. Status Solidi (a)* **15** (1973) 681.
8. J. M. TRAUTMANN and H. FORESTIER, *Comp. Rend. (Paris)* **261** (1965) 4423.
9. W. KEUNE, R. HALBAUER, U. GONSER, J. LAUER and D. WILLIAMSON, *J. Appl. Phys.* **48** (1977) 2976.
10. J. B. NEWKIRK, *J. Metals* **9** (1957) 1214.
11. A. G. GUY, "Physical Metallurgy for Engineers" (Addison-Wesley, 1962) pp. 291–324.
12. A. F. WELLS, "Structural Inorganic Chemistry", 5th Edn (Clarendon Press, Oxford, 1984) p. 1288.
13. M. HANSEN and K. ANDERKO, "Constitution of binary alloys", 2nd Edn (McGraw-Hill, New York, 1958) p. 397.
14. A. COUTURE and R. ANGERS, *Metall. Trans.* **17A** (1986) 37.

Received 3 March
and accepted 22 May 1986