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Influence of magnetic field on the reduction of hematite by hydrogen

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Measurements are reported which show that a magnetic field has very little effect on the reduction of hematite by hydrogen. Determinations of water loss indicate that the reduction rate increases by 9% in the presence of a field of 500 G. There is no further increase between 500 and 5000 G. The magnetization reflects this field dependence. Mössbauer spectra of the reduced samples clearly show the different reduction products Fe, Fe_3O_4, Fe_2O_3.

1. Introduction

Several approaches have been used to investigate the reduction of hematite (α-Fe_2O_3) by hydrogen. Previous work has dealt with the dependence of the reduction rate on total and partial pressure of hydrogen, and temperature [1, 2]. Further it has been found that the yield of the metallic ingredients is initially linear with time [3, 4].

A particularly interesting effect was indicated by Skorski [5] who carried out the reaction in the presence of a magnetic field and reported a significant increase of the speed of reduction. These results have been interpretated by Peters [6] using a thermodynamic approach. The purpose of the present work was to study the influence of a magnetic field on the reduction of hematite by hydrogen in more detail and to characterize the reaction products.

2. Experimental procedure

The reduction of hematite by hydrogen may be described by the following simplified equation:

$$Fe_2O_3 + H_2 \rightleftharpoons 2\,Fe + 3\,H_2O. \qquad (1)$$

This complete reaction takes place well above 500° C [1, 2].

The effect of reduction at lower temperatures is to provide intermediate oxides of iron, e.g. magnetite (Fe_3O_4), Wüstite (FeO), or a mixture of both with metallic iron. Moreover, Graham *et al.* have recently demonstrated that Wüstite is present only above 570° C [9].

We have monitored the reduction reaction in three ways: (1) by collecting the water given off directly; (2) by measuring the magnetic moment of the products; and (3) by using Mössbauer spectrometry to identify all the reaction products.

As raw materials we selected: (a) homogenized powder of reagent grade hematite* (Fe_2O_3); (b) hydrogen of 99.9% purity.

The experimental procedure used to measure the loss of water was similar to that used by Skorski [5].

3. Methods

A cylindrical furnace containing a pyrex tube along its axis was inserted into a magnetic field. A 5 g sample in an alumina boat was placed in the furnace and hydrogen was passed through the sample chamber, the flow (40 litre h^{-1}) being controlled by a flowmeter outlet which was more accurate than using a flame height analyser [5].

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*Supplied by Prolabo, Paris: Fe_2O_3, 99%; heavy metals, 0.01%; Cl, 0.01%; SO_4, 0.05%; loss by calcination, 0.5%.

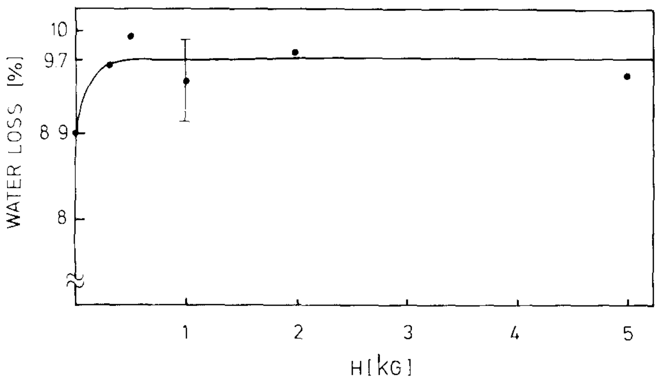

Figure 1 Dependence of the reduction of hematite by hydrogen on the intensity of magnetic field.

For the collection of water we found that the freeze-out-technique by dry ice and acetone was most convenient. Inside the sample chamber itself the temperature was regulated by means of a feedback system to better than ± 2° C. All temperatures were measured using chromel/alumel thermocouples. Before starting the reduction, the sample was annealed to 300° C for 30 min in a helium atmosphere. Behind the sample chamber a small outgassing tube was introduced in order to ensure that all the absorbed water was removed. In each run the reduction was stopped after 30 min and the sample was renewed. The electromagnet used had parallel poles of 85 mm diameter, and a gap of 52 mm.

The magnetization measurements were made on samples of about 100 mg using a vibrating sample magnetometer (see, for example [7]) in applied fields of 0 to 10 kG. For the Mössbauer spectra a standard constant acceleration spectrometer and a source of 10 mCi ^{57}Co in rhodium were used (see for example [8]).

4. Results

4.1. The observed loss of water

Measurements were carried out in magnetic fields 0 to 5 kG, and in the temperature range 180 to 320° C. After a 30 min reaction, 8.9% of the maximum possible water (Equation 1) had been evolved without the field, and 9.7% with the field at 300° C, as shown in Fig. 1. This corresponds to a 9% increase in the rate of reduction in a magnetic field with respect to the zero-field value of 8.9%. While this was observed at low magnetic fields from 0 to 500 G, no further field dependence was observed at higher fields up to 5000 G.

TABLE I Magnetization of four samples reduced without and with a magnetic field at two different temperatures. The measurements were taken in a vibrating sample magnetometer [7]

Temperature of reduction (°C)	$M(0)$ without field ($H = 0$ kG) (emu g^{-1})	$M(0)$ with field ($H = 1$ kG) (emu g^{-1})
218	5.9 (± 0.5)	6.5 (± 0.5)
300	50.9 (± 4.0)	54.7 (± 4.0)

4.2. Measurements of the magnetization

Since hematite is essentially antiferromagetic, only the reduced part consisting of Fe_3O_4 and possibly Fe can contribute significantly to the magnetization . The results of the magnetization measurements are given in Table 1. $M(H)$ was measured at room temperature in fields up to 10 kG after reduction, and the magnetic moment $M(0)$ was obtained by extrapolating to $H = 0$.

4.3. Mössbauer measurements

The study of Mössbauer spectra [9, 10] gives the possibility of picking out not only the unreduced fraction of α-Fe_2O_3 and the reduced Fe_3O_4, but also FeO and Fe if they are present in quantities greater than ~ 1%. Fig. 2 shows the spectra taken at room temperature for samples reduced at 300° C with and without a field. The data were fitted with six-line Lorentzian patterns and the hyperfine parameters which were found correspond to those of α-Fe_2O_3 and Fe_3O_4. There was no qualitative difference between the spectra with and those without field. The relative amounts of the different phases are listed in Table II. The analysis gave only 1% Fe and no FeO.

5. Discussion

We find in our measurements only a very small effect of the magnetic field on the reduction of hematite by hydrogen at 300° C. In detail, the measurements of the loss of water produced by

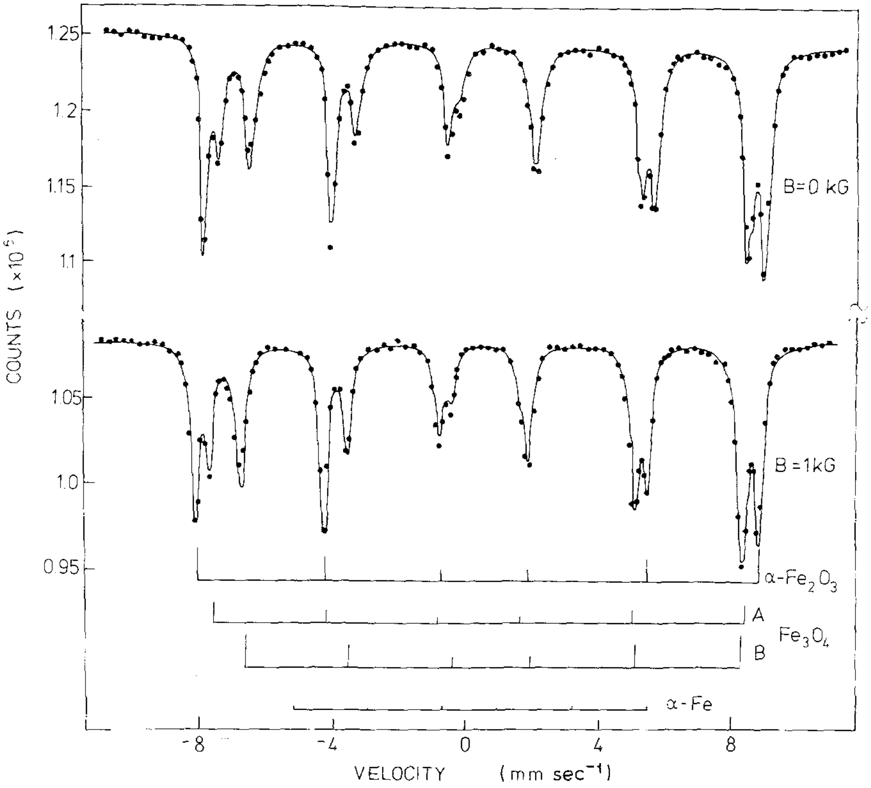

Figure 2 Mössbauer spectra for samples reduced at 300° C.

the reduction have shown that the reduction rate increases by 9% in the presence of a magnetic field of 500 G.

Our results do not confirm the high field dependence reported initially [5] and predicted theoretically [6] but are consistent within standard error with the results of [11]. There is possibly an unknown connection between the magnetic saturation of iron at ~500 G and the smoothing out of the increase of the reduction rate above that value.

Analysis of the reduced samples carried out with a magnetometer confirmed that there is only a small field dependence. The Mössbauer spectra of the reduced sample clearly show the different reduction products. Computer analysis of the spectra shows that the percentage of the various components changes little with the applied field.

TABLE II Percentage of different reduction products at 300° C as analysed by computer from the Mössbauer spectra

	Fe_3O_4 (%)	Unreduced fraction α-Fe_2O_3 (%)	Fe(%)	FeO(%)
$B = 1$ kG	63 (± 4)	36 (± 3)	1 (± 1)	–
$B = 0$ kG	57 (± 4)	42 (± 3)	1 (± 1)	–

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