Mechanochemical treatment of α-Fe₂O₃: a neutron diffraction study

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Abstract. In agreement with earlier studies, neutron diffraction measurements show that off-stoichiometric $Fe_{3-x}O_4$ is the main product of wet-milling haematite, α-Fe_2O_3, in vacuum with defect magnetite, $\sim Fe_{2.8}O_4$, being obtained after milling for 72 and 144 h. Rietveld refinements of the room-temperature neutron diffraction patterns show that $\sim Fe_{2.8}O_4$ exhibits reduced lattice parameters ($\sim 0.1\%$) and magnetic moment values ($\sim 5\%$) compared with stoichiometric Fe_3O_4. Comparison of the Fe_2O_3 content as determined from the phase fractions of the 72-h milled sample ($\sim 7\%$) and following heat treatment at ~ 950 K ($\sim 37\%$) reveals that a significant fraction of α-Fe_2O_3 is present in the milled product in an amorphous-like or disordered state.

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The effects of milling α-Fe_2O_3 under a variety of environments and milling conditions have been investigated by a number of workers (e.g. [1–7]). Of particular interest are the transformation of α-Fe_2O_3 to cation-deficient magnetite, $Fe_{3-x}O_4$, that occurs when haematite is wet-milled in vacuum under low-energy milling conditions [1,4] and the possible role that γ-Fe_2O_3 plays in the overall effectiveness of the transformation.

Following our earlier room-temperature neutron diffraction investigation of a sample of α-Fe_2O_3 wet-milled in vacuum for 200 h [6], we here investigate the products of α-Fe_2O_3 wet-milled for 72 and 144 h using in-situ neutron diffraction measurements at temperatures up to ~ 950 K. These milling times were selected to match the period of ~ 144 h over which the transformation from haematite to magnetite has been investigated systematically [1]. Rietveld refinements enable the phase fractions of $Fe_{3-x}O_4$ and other oxide phases present in the milled products to be determined. In the present paper emphasis is placed on the analysis and evolution of the distribution of the oxide phases in the sample milled for the intermediate time of 72 h.

1 Experiment

The starting charge of α-Fe_2O_3 (purity 99.99%, particle size distribution in the range of 20–70 μm , Koch-LightLaboratories) was wet-milled in vacuum in a vertical stainless-steel mill as outlined previously [4, 6]. The material was milled for periods of 72 and 144 h in the low-energy mode. The room-temperature neutron diffraction measurements were carried out on the time-of-flight LAD diffractometer, ISIS, UK, with the high-temperature measurements (~ 300–950 K) carried out on the E6 diffractometer ($\lambda = 2.445$ Å) at HMI, Berlin. The diffraction patterns were analysed by Rietveld refinement using the programme package GSAS, which allows simultaneous refinement of nuclear and magnetic contributions.

2 Results and discussion

Figure 1 shows as an example the diffraction pattern for the 144-h milled sample with the results of Rietveld refinements given in Table 1. In agreement with earlier studies (e.g. [1, 4–6]), two main phases – off-stoichiometric *fcc* $Fe_{3-x}O_4$ spinel-type and rhombohedral α-Fe_2O_3 – are observed in the as-milled sample. Additionally, the refinements reveal that up to $\sim 2\%$–3% α-Fe is present in the milled samples (resulting from milling in the stainless-steel container), although for convenience in the analysis and discussion these small fractions are not included in the table. The refinements were carried out on the basis that the vacancies exist in the energetically more favourable octahedral Fe^{2+}/Fe^{3+} sites rather than the tetrahedral Fe^{3+} sites, leading to the vacancy values for nonstoichiometric $Fe_{3-x}O_4$ given in Table 1. The apparent phase fractions of $Fe_{3-x}O_4$ increased from ~ 90 to $\sim 96\%$ when the milling time was extended from 72 to 144 h, similar to the behaviour observed earlier in an X-ray diffraction investigation [1]. The XRD patterns revealed that the rate of transformation from haematite to magnetite on milling was

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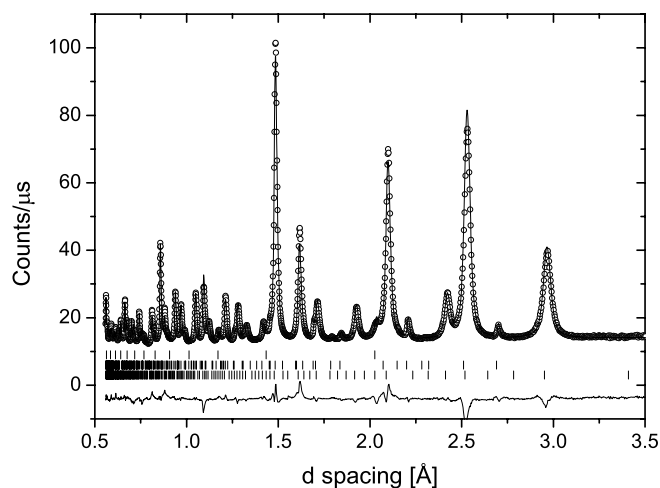
Fig. 1. Room-temperature time-of-flight neutron diffraction pattern and Rietveld refinement for the α-Fe$_2$O$_3$ sample wet-milled for 144 h. The phase markers are: α-Fe (*top*), Fe$_{3-x}$O$_4$ (*middle*) and α-Fe$_2$O$_3$ (*bottom*)

	Fe$_{3-x}$O$_4$	α-Fe$_2$O$_3$	Fe$_{3-x}$O$_4$	α-Fe$_2$O$_3$
Time (h)	72	72	144	144
Fraction (%)	90 (1)	7 (1)	96 (1)	3 (1)
a (Å)	8.3876 (1)	5.429 (2)	8.3845 (2)	5.430 (2)
α (°)	–	55.27 (2)	–	55.25 (2)
M (μ_B)	–	3.9 (1)	–	3.4 (3)
$M_{(tet.)}$	4.19 (4)	–	4.12 (6)	–
$M_{(oct.)}$	3.88 (5)	–	3.50 (5)	–
x	0.15 (1)	–	0.21 (1)	–

Table 1. Results of Rietveld refinements for α-Fe$_2$O$_3$ samples wet-milled for 72 and 144 h

highest during the first few hours; it decreased thereafter. This behaviour is due to reduction in the transferred energy density that is a result of the increase in surface area with decreasing particle size during continuous milling.

Analysis of the peak broadening (as part of the Rietveld refinement) led to mean crystallites sizes for Fe$_{3-x}$O$_4$ in both of the milled samples of $\langle D \rangle \sim 45(10)$ nm with isotropic microstrain values of $\Delta a/a \sim 0.3\%$. The particle sizes agree well with recent SEM measurements which show size distributions centred around ~ 50 nm [8]. In addition, a fraction of particles with average sizes $\gtrsim 100$ nm can be linked with the presence of unreacted α-Fe$_2$O$_3$ in the milled products. As indicated in Table 1, the refinements show that defect Fe$_{3-x}$O$_4$ has reduced lattice parameters ($\sim 0.1\%$) and magnetic moment values ($\sim 5\%$) compared with those of stoichiometric Fe$_3$O$_4$ [9].

As noted above, the apparent phase fractions of Fe$_{3-x}$O$_4$ in the samples milled for 72 and 144 h are ~ 90 and $\sim 96\%$ respectively (Table 1). However, an important point to note is that these latter values are derived from the crystalline-like peaks present in the diffraction patterns of the milled products (e.g. Fig. 1). As such they do not take proper account of either amorphous Fe$_2$O$_3$ contributing to the diffuse background scattering or residual α-Fe$_2$O$_3$, which remains undetected because of the peak broadening due to size and strain effects. Given the similarity in crystal structural parameters between Fe$_3$O$_4$ and γ-Fe$_2$O$_3$, a further factor is the possible presence of γ-Fe$_2$O$_3$. In order to clarify these points, additional in-situ

high-temperature measurements were carried out at ~ 950 K on the milled products. The heat treatment was carried out in high vacuum to prevent any Fe$_3$O$_4$ from being oxidised to Fe$_2$O$_3$. The temperature of ~ 950 K was selected as it is well above both the transformation temperature from γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$ and the Curie and Néel temperatures of the oxide phases.

Several points can be noted from the series of diffraction patterns for the 72-h milled sample shown in Fig. 2. There is a significant reduction in the background scattering both at ~ 950 K (Fig. 2b) and on re-cooling to room temperature (Fig. 2c) compared with the as-milled sample (Fig. 2a). This is consistent with recrystallisation of amorphous or disordered components of the milled products as also indicated by the relatively narrow peaks in Fig. 2b and c compared with those in Fig. 2a. Refinement shows that the fraction of α-Fe$_2$O$_3$ present in the recrystallised milled sample (Fig. 1c) has increased significantly from $\sim 7\%$ in the as-milled state (Fig. 2a) to ~ 37 (2)% after heating in vacuum to ~ 950 K. Based on these findings, it is clear that the majority of the Fe$_2$O$_3$ phase (α or γ) exists in an amorphous or
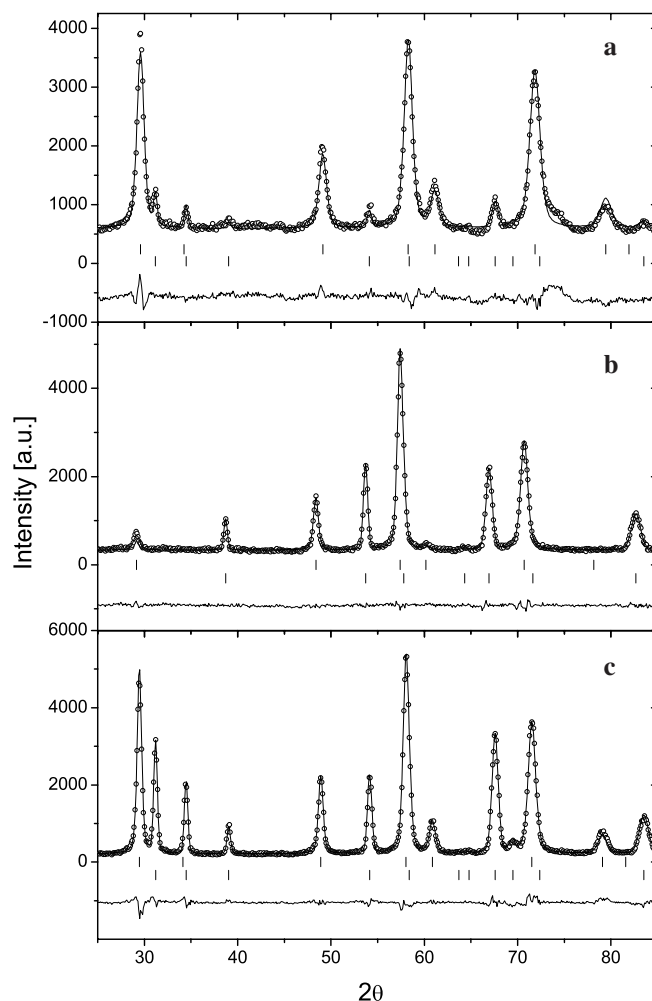

Fig. 2. Constant-wavelength neutron diffraction patterns and Rietveld refinements for α-Fe$_2$O$_3$ wet-milled for 72 h: **a** as-milled at room temperature; **b** in situ at ~950 K; **c** at room temperature after exposure to ~950 K. The phase markers are: Fe$_{3-x}$O$_4$ (*top*) and α-Fe$_2$O$_3$ (*bottom*)

nanostructured/disordered form, thus contributing to the diffuse neutron scattering observed in the as-milled samples.

Previous investigations of the effects of milling oxides reported significant fractions of γ-Fe_2O_3 in the milled products (e.g. [3, 10]). By comparison, there is little direct evidence for the occurrence of γ-Fe_2O_3 in the present investigation. While γ-Fe_2O_3 can be generally described as having the spinel structure of the lattice parameter slightly reduced compared with that of Fe_3O_4, it nonetheless has a unique ordered vacancy distribution in the octahedral sites [11, 12], leading to satellite peaks in the diffraction patterns. While such superstructure lines were observed in the diffraction patterns of an α-Fe_2O_3 sample wet-milled for 200 h using the high-intensity diffractometer POLARIS (of higher resolution than LAD) [6], no evidence for the presence of satellite peaks was obtained in the present experiments using LAD. However, some insight to the possible presence of γ-Fe_2O_3 in the milled samples can be obtained by comparing the integrated intensities of peaks which, because of the similarity in lattice parameters, may be due to Fe_3O_4 or to γ-Fe_2O_3. For example, comparison of the intensities of the peak located at the (2 2 0) position (at $2\theta \sim 48.9°$) of Fe_3O_4 before (Fig. 2a) and after exposure to ~ 950 K (Fig. 2c) reveals a decrease in intensity of $\sim 8\%$. This suggests that should γ-Fe_2O_3 be present in crystalline form in the milled sample, it could contribute a maximum of only $\sim 8\%$–10% in the milled product. It is therefore concluded that the majority of the Fe_2O_3 (α or γ) phase originates from the amorphous/disordered region.

3 Conclusions

Neutron diffraction measurements have confirmed the transformation of α-Fe_2O_3 to $Fe_{3-x}O_4$ on wet milling in vacuum. A phase fraction of only $\sim 7\%$ of α-Fe_2O_3 is obtained on refinement of the reflections in the 72-h wet-milled sample, whereas analysis of the sample following heating at ~ 950 K shows the presence of $\sim 37\%$ of the α-Fe_2O_3 phase in the heat-treated state. This latter value indicates that the unreacted α-Fe_2O_3 exists in an amorphous-like or disordered form. While there is no direct evidence for the presence of γ-Fe_2O_3, via, say, the occurrence of vacancy superstructure lines [11, 12], comparison of room-temperature patterns before and after treatment at ~ 950 K indicates a maximum fraction of $\sim 8\%$–10% γ-Fe_2O_3 in the milled product. The occurrence of such a maghemite phase is related to the damaged surface layer of particles in the as-milled state (comparable effects of disordered and nonstoichiometric surface behaviour have previously been found for both magnetic spinels and hexagonal ferrites by high-resolution SEM [13]). We conclude that the γ-Fe_2O_3 fraction ratio does not appear to play a significant role in the mechanochemical transformation of α-Fe_2O_3 to $Fe_{3-x}O_4$.

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