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Preparation and investigation of magnetic properties of wüstite nanoparticles

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ABSTRACT

In this work wüstite nanoparticles have been prepared via high-energy ball milling, using high-purity hematite (Fe_2O_3) and iron (Fe) powders as the starting materials. In order to get a single-phase wüstite different mole ratios of (Fe/Fe_2O_3) were milled, using a planetary mill. X-ray diffraction studies of the as-milled powders show that a single-phase wüstite was formed for a mole ratio of 0.6. Lattice parameter of the wüstite was obtained from XRD data, by which a value of 0.072 was obtained for x in $Fe_{1-x}O$. A mean crystallite size of 13 ± 1 nm was calculated for the single-phase wüstite, using Scherrer's formula. The morphology of the powders was also checked by TEM. Variations of pressure and temperature in the vial were recorded with respect to the milling time, using a GTM unit. Hysteresis loops of the as-milled powders at 5 K and room temperature have been obtained by SQUID and by VSM systems, respectively. The loops show non-zero coercivity, in contrast to the bulk wüstite. The observed magnetizations can be explained by a model based on the spinel-type defect clusters in non-stoichiometry wüstite.

1. Introduction

There are four major iron oxide phases, which consist of FeO, Fe_3O_4, γ-Fe_2O_3 and α-Fe_2O_3, and are named wüstite, magnetite, maghemite and hematite, respectively. In these oxides, wüstite is almost nonstoichiometric with some Fe deficiency and can be denoted as $Fe_{1-x}O$. Apart from wüstite, other iron oxide phases are very important technologically and have many applications in different industries. Nevertheless wüstite is very interesting on its own: for example, its unusual electronic properties. $Fe_{1-x}O$ is an interesting semiconductor whose carrier type changes from p to n type around $x = 0.08$ [1]. On the other hand from the viewpoint of magnetic properties, stoichiometric FeO is an antiferromagnet with a Neél temperature of about 200 K and has a rock salt structure, with a closed-packed fcc O^{2-} lattice in which Fe^{2+} ions occupy the octahedral (B) interstitial sites [2].

In order to preserve the total crystal electroneutrality of $Fe_{1-x}O$, some of the Fe^{2+} ions give away another electron and become Fe^{3+}. This means that for a particular value of x, there are $2x Fe^{3+}$ and $(1-3x)$ Fe^{2+} ions and this iron deficiency leads to the formation of some vacancies. These vacancies are partly located as Frenkel defects on interstitial tetrahedral sites [3–9].

Neutron-diffraction [3–5,9] and X-ray-scattering [4] studies on quenched $Fe_{1-x}O$ powders and single crystal $Fe_{1-x}O$ indicate that the vacancies are not randomly distributed but clustered around Fe^{3+} ions. These Fe^{3+} ions preferentially occupy the tetrahedral (A) interstitial sites.

Significant progress towards understanding the possible structure of a defect cluster has been achieved in the theoretical work of Catlow and Fender [7]. In this work they have suggested that the basic cluster is identified as a complex of four cation vacancies and one tetrahedral Fe^{3+} ion (or 4:1 cluster) (Fig. 1(a)). This cluster is formed as a result of a large Coulomb energy term favoring the occupation of the tetrahedral site when all nearest-neighbor cations are vacant. The aggregation of these 4:1 clusters occurs by vacancy sharing and the calculations suggest that the most stable small aggregates are formed by edge sharing rather than corner-sharing (6:2 or 8:3 clusters). If more extended clusters are formed they are likely to involve corner-sharing, but the binding energy for a cluster closely related to the inverse spinel structure of Fe_3O_4 (16:5) (Fig. 1(c)) is larger than that calculated for the Koch-Cohen cluster (13:4) (Fig. 1(b)) [4]. Koch and Cohen (1969) by using X-ray studies, deduced that defects in $Fe_{1-x}O$ are aggregated to the order of 13:4 cluster (13 octahedral

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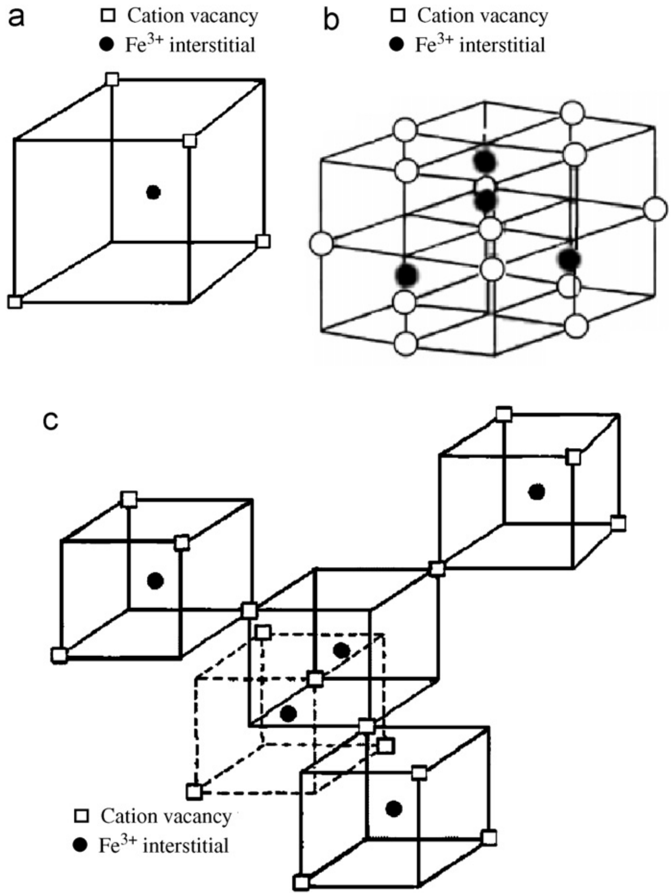

Fig. 1. (a) 4:1 cluster; (b) Koch and Cohen cluster; (c) 16:5 spinel-like cluster.

vacancies surrounding 4 tetrahedral Fe^{3+}) with a noticeable displacement of ions near the cluster and that the defect does not quite have the Fe_3O_4 structure (Fig. 1(c)). Catlow and Fender studies have been supported by the neutron diffraction works of Cheetham et al. and Battle et al. [5,9].

Recently, anomalous high magnetization and low-temperature coercivity were found in sputtered $Fe_{1-x}O$ films [10,11]. In the recent works, defect clusters in $Fe_{1-x}O$ films and their ferrimagnetism properties have been reported by Dimitrov et al. [12,13].

Although wüstite exists in nature, there are different physical and chemical methods to prepare it [5,9,14–16]. One of the most attractive physical methods is high-energy ball milling (HEBM). HEBM is a powerful process to synthesize metastable materials such as amorphous alloys and nanocrystalline materials [17–20].

An earlier report on the formation of non-equilibrium phases in the Fe–O system via HEBM has been published in 1991 [21]. Matteazziand and Le Caër found HEBM of Fe_2O_3 and carbon resulted in the formation of magnetite and wüstite. The formation of metastable wüstite phase via HEBM of Fe/Fe_3O_4 has been reported by Ding et al. [22]. Milling of an equimolar mixture of Fe_3O_4 and Fe for 20 h resulted in formation of the wüstite phase, with a minor phase of α-Fe. They also milled Fe_2O_3 and Fe mixture, and a wüstite together with a trace of Fe was found after 20 h milling. Also they observed that with longer milling time, a pure wüstite phase is achievable [23]. Ding et al. [24] milled zFe. $(1-z)$ Fe_2O_3 mixture, with $0<z<1$, for 30 h and found that the milled powders consisted of Fe_3O_4 and FeO for $z = 0.2–0.5$, and consisted of FeO and Fe for $z \geqslant 0.5$. Then nanocrystalline metastable FeO decomposed into nanocrystalline Fe_3O_4 and Fe after annealing at 250–400 °C and reformed again to FeO after annealing at temperatures above 550 °C. Bonetti et al. [25] milled a mixture of Fe_3O_4 and Fe for 50 h and then annealed the as-milled powders for 1 h at 600 °C. They found a high fraction of wüstite (80 wt%) in the final product.

In this work we have used HEBM to prepared FeO by a mixture of Fe and α-Fe_2O_3 and investigated its magnetic properties at room and low temperatures.

2. Experimental

To prepare each sample a mixture of 30 g of the raw materials (Fe powder from Merck Co. with minimum purity of 99% and a refined α-Fe_2O_3 from a domestic source with a purity of 99.85% [26]) were used. Desirable Fe/Fe_2O_3 mole ratios (from 0.6 to 1 by a step of 0.1) together with 270-g hardened steel balls of different sizes were loaded into a 500 cc volume hardened steel vial. The milling was performed for 20 h in air in a high-energy planetary mill (Fritsch, Pulverisette 6) with a rotational speed of 500 rpm. In order to determine iron wear in the course of milling, the weight of balls and vial were carefully weighed before and after milling. To investigate variations of temperature and pressure in the vial during the milling process, a GTM unit (Fritsch) was used. The unit is capable of sending the data from a transmitter's antenna (fixed on the top of the vial) to the receiver connected to a computer. Special software, named GTM II, was used to record the temperature and the pressure as a function of the milling time.

The crystal structure of the as-milled powders was studied by an X-ray diffractometer (Bruker Advanced D8 model), using CuKα radiation ($\lambda = 1.5406$ Å). The microstructure and particle size of the powders were examined by a transmission electron microscope (TEM), Philips CM12 model. Magnetic measurements were made at room temperature, using a vibrating sample magnetometer (VSM) with a maximum applied field of 10 kOe, and at low temperature, using a SQUID magnetometer with a maximum applied field of 50 kOe.

3. Results and discussion

Based on the following chemical reaction

$$Fe + Fe_2O_3 \rightarrow 3FeO$$

it is necessary to choose an equimolar of Fe and Fe_2O_3 to get a single-phase FeO. But XRD investigations of the as-milled powders with different mole ratios show that only the sample with a mole ratio 0.6 is a single-phase wüstite (Fig. 2(a)) and for higher mole ratios the products are iron–wüstite composites. Fig. 2(b) shows the XRD pattern of the sample with a mole ratio 1, as a typical example of the XRD pattern of samples with higher than mole ratio 0.6. The reason of using a mole ratio of 0.6 (obtained experimentally) instead of equimolar one is due to iron uptake in the course of milling.

Also according to the relation $a = 4.334–0.478x$ [27] and the unit cell parameter of $Fe_{1-x}O$ ($a = 4.2998$ Å) obtained from XRD pattern, the x value is 0.072. As can be seen the main peaks observed at diffraction angles of 36.1, 42.1 and 60.9 correspond to wüstite ($Fe_{1-x}O$). An average crystallite size of 13 ± 1 nm has been obtained for the single-phase sample, using Scherrer's formula [28].

Fig. 3 shows the variations of pressure and temperature in the air-filled vial in the course of milling as functions of time. As can be seen, the pressure rises sharply in the first 20 min and reaches a maximum value of about 90.6 ± 0.1 kPa. There are two reasons for this pressure increase. First, it is related to the released oxygen due to the following chemical reaction [16]:

$$Fe_2O_3 \rightarrow Fe_2O_{3-\delta} + 1/2\delta O_2$$