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 (Fe₂O₃) and iron (Fe) powders as the starting materials. In order to get a single-phase wüstite different molar ratios of (Fe/Fe₂O₃) 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 molar ratio of 0.6. Lattice parameter of the wüstite was obtained from XRD data, by which a value of 0.072 was obtained 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 5K 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.

Keywords:
Wüstite nanoparticle
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1. Introduction

There are four major iron oxide phases, which consist of FeO, Fe₂O₃, γ-Fe₂O₃, and δ-Fe₂O₃, 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 Fe₁₋ₓO. 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. Fe₁₋ₓO 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 O²⁻ lattice in which Fe³⁺ ions occupy the octahedral (B) interstitial sites [2].

In order to preserve the total crystal electroneutrality of Fe₁₋ₓO, some of the Fe²⁺ ions give away another electron and become Fe¹⁺. This means that for a particular value of x, there are 2Fe²⁺ and (1-3x)Fe³⁺ 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 Fe₁₋ₓO powders and single crystal Fe₁₋ₓO indicate that the vacancies are not randomly distributed but clustered around Fe³⁺ ions. These Fe³⁺ 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 Fe³⁺ 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 Fe₂O₃ (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 Fe₁₋ₓO are aggregated to the order of 13:4 cluster (13 octahedral
Matteazzi and Le Cær found HEBM of Fe$_2$O$_3$ and carbon in the Fe–O system via HEBM has been published in 1991 [21].

The formation of FeO and Fe for $z$ decomposed into nanocrystalline Fe$_3$O$_4$ and Fe after annealing at temperatures above 550 °C. Ding et al. reported by Ding et al. [22]. Milling of an equimolar mixture of Fe$_3$O$_4$ and Fe for 20 h resulted in formation of the wüstite phase, such as amorphous alloys and nanocrystalline materials [17–20].

HEBM is a powerful process to synthesize metastable materials and chemical methods to prepare it [5,9,14–16]. One of the most attractive physical methods is high-energy ball milling (HEBM).

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$_2$O$_3$ and carbon resulted in the formation of magnetite and wüstite. The formation of metastable wüstite phase via HEBM of Fe/Fe$_2$O$_3$ has been reported by Ding et al. [22]. Milling of an equimolar mixture of Fe$_3$O$_4$ and Fe for 20 h resulted in formation of the wüstite phase, with a minor phase of $\alpha$-Fe. They also milled Fe$_2$O$_3$ 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 $z$Fe. (1–$z$) Fe$_2$O$_3$ mixture, with 0<$z$<1 for 30 h and found that the milled powders consisted of Fe$_3$O$_4$ and FeO for $z$=0.2–0.5, and consisted of FeO and Fe for $z$>0.5. Then nanocrystalline metastable FeO decomposed into nanocrystalline Fe$_3$O$_4$ 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$_2$O$_3$ 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 $\alpha$-Fe$_2$O$_3$ 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 $\alpha$-Fe$_2$O$_3$ from a domestic source with a purity of 99.85% [26]) were used. Desirable Fe/Fe$_2$O$_3$ 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 20h 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 CuK$_\alpha$ 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

$$\text{Fe} + \text{Fe}_2\text{O}_3 \rightarrow 3\text{FeO}$$

it is necessary to choose an equimolar of Fe and Fe$_2$O$_3$ 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 Fe$_3$O$_4$ ($d_0=4.2998$ Å) obtained from XRD pattern (obtained experimentally) instead of Fe$_2$O$_3$ ($d_0=4.334$ Å) respectively.

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]:

$$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_2\text{O}_{3-x} + 1/2\text{O}_2$$

Fig. 1. (a) 4:1 cluster; (b) Koch and Cohen cluster; (c) 16:5 spinel-like cluster.
where $\delta$ refers to the extent of oxygen vacancy and second, it is related to increase in temperature, mainly due to iron oxidation in the presence of the oxygen and conversion of mechanical energy into thermal energy. A sharp increase in temperature in the first 100 min confirms this hypothesis. As can be seen in Fig. 3, in a time interval of 20–120 min, the pressure decreases sharply. This is due to the reaction of vacant iron oxide, oxygen and iron, based on the following reaction:

$$\text{Fe}_2\text{O}_3 - \delta \text{O}_2 + \text{Fe} \rightarrow 3 \text{ Fe}_{1-\delta}\text{O}$$

which leads to formation of wüstite. As time is passing the thermal energy due to mechanical energy conversion leads to an increase in temperature and then it reaches a constant value after 5 h, due to a thermal equilibrium condition. As can be seen the pressure also has the same behavior.

Fig. 4 shows the TEM micrograph of the single-phase wüstite. The average size of the particles in the aggregates is in the range of the crystallite size obtained by Scherrer’s formula.
Fig. 5 shows the hysteresis loops of the single-phase wüstite at room temperature and at 5 K. As can be seen, both curves show non-zero coercivities and remanence magnetizations in the form of ferrimagnetic behavior. The same behavior has been observed for wüstite thin film at low temperatures (10 K) [13, 14]. Magnetizations have not been saturated even in a field of 50 and at 5 K temperature. Magnetizations are 11 and 20 emu/g in applied fields of 9 and 50 kOe respectively. This is in contrast to the behavior of bulk wüstite, which is antiferromagnetic at temperatures below 200 K (its Neél temperature) and paramagnetic above it [2].

According to Dimitrov et al. [13, 14], the observed magnetization can be due to the spinel-type defect clusters (Fig. 1(c)). Based on these works, it is possible to consider that defect clusters in our sample may comprise a Fe$_3$O$_4$-like phase coherently embedded in an ideal FeO matrix. Then for a particular value of $x$ in Fe$_{1-x}$O, there are $x$ molecules of Fe$_3$O$_4$ and $(1-4x)$ molecules of FeO. Then in our sample there are 0.712 molecules of FeO and 0.072 molecules of Fe$_3$O$_4$, which can be the cause of observed hysteresis loops.

4. Conclusion

Wüstite single phase was obtained simply by mechanical milling of Fe and Fe$_2$O$_3$. The nanosized prepared wüstite shows ferromagnetic-like behavior, which was interpreted according to spinel-like defect clusters.

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References