

Magnetite microcrystals for magneto-rheological fluids

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Abstract

We report a new synthetic method for the preparation of micrometric prismatic crystals of magnetite by means of a coprecipitation reaction of aqueous solutions of iron salts and ammonium oxalate, followed by thermal decomposition of the precipitate in an inert atmosphere. Magnetite prismatic crystals grown by this procedure are homogeneous in size and morphology. We also study the structure and orientation of the magnetic domains.

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1. Introduction

Magneto-rheological fluids (MR) are materials composed by micrometric (0.1–100 μm of diameter) magnetic particles, dispersed in an inert fluid, usually a mineral oil [1]. The rheological properties of these complex materials change drastically under the application of a magnetic field as much as they can undergo a reversible liquid-to-solid transition due to the complex structure formed by the particles. In the case of MR fluids, the particles used are usually iron powders, manganese zinc ferrite, nickel zinc ferrite [2–4]. Magnetite, Fe_3O_4 , is one of the most interesting iron oxides due to its magnetic properties. The Curie temperature is 580 °C and the saturation magnetization at room temperature, j_s is 480 G [5]. The crystal structure is of the type of inverse spinel [6], where cations are distributed between the A and B sublattices, the two B sites per unit formula are occupied by one Fe^{2+} and one Fe^{3+} , and the A site is occupied by the remaining Fe^{3+} . The cations magnetic moments within each sublattice are parallel coupled, whereas A and B sublattices are antiparallel coupled. Due to the fact that the sublattice B has one Fe^{2+} and one Fe^{3+} for every Fe^{3+} cation in the A

sublattice, the atomic moments of the Fe^{3+} cancel out, leaving a net magnetic moment due to the Fe^{2+} cations. This antiparallel coupling of two unequal sublattices makes Fe_3O_4 ferrimagnetic. The easy direction of magnetization is [111]. It is known in synthetic work that in the iron–oxygen phase diagram, hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) compete with the magnetite phase [7,8].

The oxidation of magnetite yield maghemite, in this compound the inverse spinel structure is preserved, but all cations are Fe^{3+} and the atomic moments are parallel coupled, but approximately antiparallel coupled between adjacent layers of cations. However, the angle between magnetic moments of these alternate layers departs slightly from 180°, this type of magnetization is referred as canted antiferromagnetism [9]. The presence of cation vacancies decreases saturation of magnetization from 480 G for magnetite, to 420 G for maghemite. Maghemite is metastable and changes irreversibly to hexagonal $\alpha\text{-Fe}_2\text{O}_3$.

Micrometric and nanometric magnetite crystals have been prepared by several procedures involving aqueous media or suspensions [7,10,11]. The source of iron used in these studies was iron (II) chloride, iron (II) acetate, iron (II) sulphate or iron hydroxide. In addition, when OH was present in excess, a cubic crystal habit was developed [10].

In the present study we report the synthesis of micrometric prismatic crystals of magnetite by coprecipitation of aqueous solutions of iron (III) nitrate, iron (II) chloride and ammonium oxalate, followed by thermal

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decomposition of the precipitates in an inert atmosphere. The produced particles have the appropriate characteristics to prepare MR, as will be shown by the results of the structural, morphological and thermal characterization obtained by X-ray diffraction (XRD), scanning electron microscopy (SEM), polarized light microscopy (PLM) and simultaneous differential thermal analysis–thermogravimetry (SDT).

2. Experimental

Solutions of iron (III) nitrate 0.1 M, ammonium oxalate 0.1 M and iron (II) chloride 0.4 M, were prepared as starting solutions. By mixing three parts of ammonium oxalate, one part of iron nitrate and two parts of iron chloride fresh aqueous solutions, we prepared the so called base solution. With this one we proved different conditions of aging of the mixture, considering that the equilibrium of ferrous and ferric ions in oxalic acid solutions is a function of pH and oxalic acid [12]. We add oxalic acid in excess to promote the precipitation. Once we obtain the precipitates, they were heated up to 800 °C in nitrogen atmosphere in order to determine the conditions to achieve their complete thermal decomposition. Morphological studies of SEM and transmitted polarized light studies of magnetic domains in the resulting microcrystals were done. XRD patterns were obtained in a D5000 Powder Diffractometer (Bruker AXS), Cu–K α radiation, $\lambda = 1.5406 \text{ \AA}$, 2θ range from 5 to 70°, step scan 0.02°, at room temperature. SEM micrographs were obtained in a JSM 5400 LV (Jeol) system. PLM studies were performed with a Universal Polarizing Microscope (Zeiss); SDT analysis were done in a simultaneous differential technique module (SDT-TA Instruments 2960), in nitrogen atmosphere with a flux of 88 cm³/min, heating rate 10 °C/min. Magnetic transition temperature was determined in the same module SDT, with the permanent magnet positioned

over the furnace. Curie temperature calibration of the system was performed using Ni reference material.

3. Results and discussion

3.1. Preparation of microcrystals

The products of the coprecipitation reaction were pale and bright yellow powders Fig. 1 shows one representative XRD pattern. We identify the presence of hydrated iron oxalates $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, and also traces of oxalic acid.

Fig. 2 shows the DTA-TG curves for these hydrated oxalates under nitrogen atmosphere up to 800 °C. In these curves it is clearly evident that the thermal decomposition process had two steps, both of them endothermic; the weight loss measured for the first one, with onset at 180 °C, corresponds to the decomposition of ferrous oxalate [13] according to the following reaction: $\text{FeC}_2\text{O}_4 \rightarrow \text{FeCO}_3 + \text{CO}$, whereas the weight loss for the second step, with onset temperature at 373 °C, can be associated to the thermal decomposition of the ferric oxalate [13]. However, in this second step one observes that the endothermic peak has two components. It means that the process is more complex than just a single reaction, we propose two consecutive reactions: $\text{FeCO}_3 \rightarrow \text{FeO} + \text{CO}_2$ followed by $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{CO}_2 + 3\text{CO}$, this assumption is based in the good agreement between theoretical calculations and experimental weight loss measurements, considering these reactions. These decomposition reactions have been also studied in related work done on iron minerals [14].

The decarbonation is a topochemical process, in order that the reaction to proceed from the surface towards the center of the crystal, it is necessary that CO_2 be capable of diffusing through the crystal structure. The surrounding pressure plays an important role. At ambient pressure,

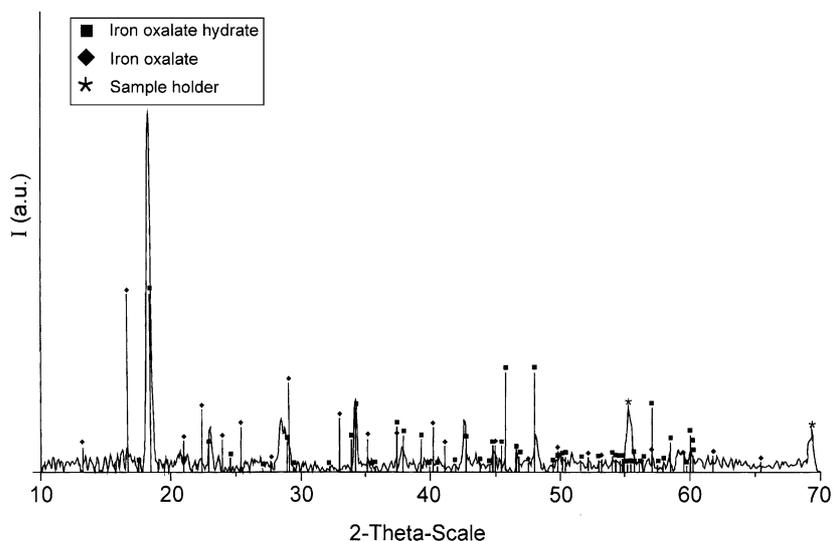


Fig. 1. XRD pattern of precipitates.

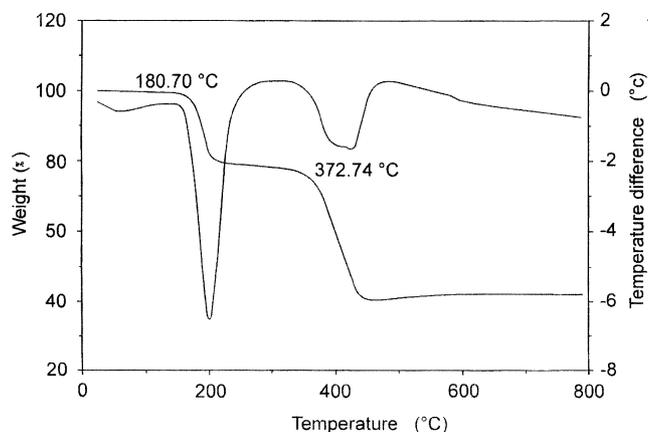


Fig. 2. DTA-TG curves of hydrated oxalates.

because of a smaller pressure gradient, CO_2 further dissociates to CO inside the crystal lattice in order to process the decarbonation, allowing only CO to diffuse out the crystal. The oxygen ion dissociated from CO_2 within the crystal lattice also provides a convenient source for the oxidation of iron oxides. The formation of magnetite could take place by one of the following known reactions [15]:

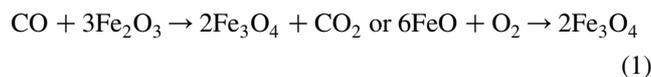


Fig. 3 shows the XRD pattern of the products of thermal decomposition. By comparison with powder diffraction files (JCPDF) for several iron oxides, we found that it corresponds to magnetite. It is very difficult to identify between maghemite (space group $P4_132$) and magnetite (space group $Fd3m$) because of their similar structures. However, analyzing the peaks corresponding to $hk0$ ($h+k=4n$), typical of d glide planes in magnetite, allows to distinguish it. These peaks are centered at $2\theta=30.10$ and 62.52° .

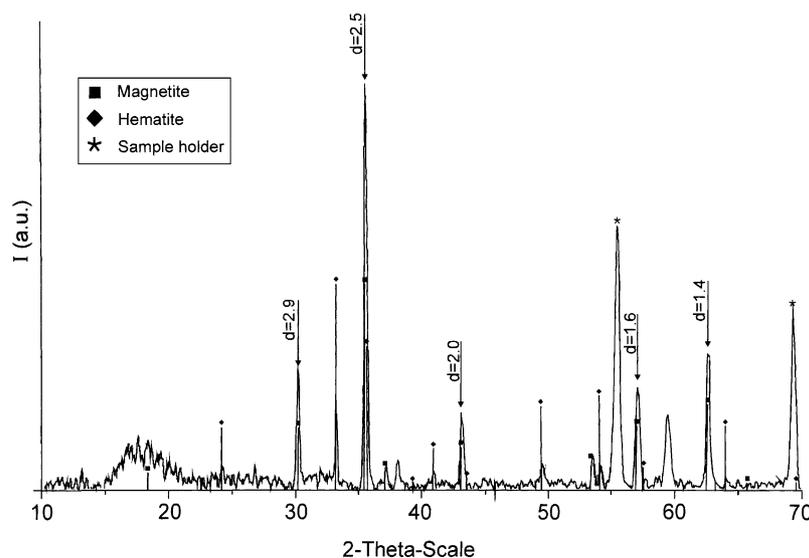


Fig. 3. XRD pattern of products of thermal decomposition.

3.2. Magnetic temperature measurement

Fig. 4 shows a thermogravimetric analysis (TGA) curve measured under the presence of magnetic field, for microcrystals obtained by the method described in the foregoing paragraph. The weight change detected in TGA curve is apparent, it is created by the change in attraction to a magnetic field, and can be used to monitor the magnetic character of a sample. Curie temperature (T_c) measured in our crystals is 578°C , that matches with the reported in literature for magnetite [5]. The importance of the measurement of Curie temperature lies in the fact that it allows to distinguish between magnetite and hematite, because the latter has T_c at 680°C [5].

Fig. 5 shows a SEM photograph of microcrystals, the size ranges between 15 and $20\ \mu\text{m}$. Crystal habit observed can be described as elongated prismatic. This morphology was reported also for magnetite prepared by decomposition of siderite (FeCO_3) [16] and it is not very common, as well as occurs with the habit of magnetite of biological origin [17]. Typical morphology of mineral magnetite is octahedral, but rarely it grows developing a rhombo-dodecahedron habit [18].

In connection with the morphology of the crystals, it is well known that the final habit developed by the crystals grown in solution, depends mainly on variables such as the concentration of the reacting components, pH, the nature of the anions present and the rate of oxidation [10]. Magnetite crystals formed in excess of OH^- are of cubic morphology [10], instead the crystals grown with different initial ratio $R=[\text{Fe}^{2+}]/[\text{OH}^-]$ show octahedral habit ($R \leq 0.5$) or hexagonal mosaic platelets ($R > 0.5$) [11].

Considering that in our procedure of preparation of magnetite in which the first stage we obtain a mixture of crystalline prismatic iron (II) and iron (III) oxalates, it seems

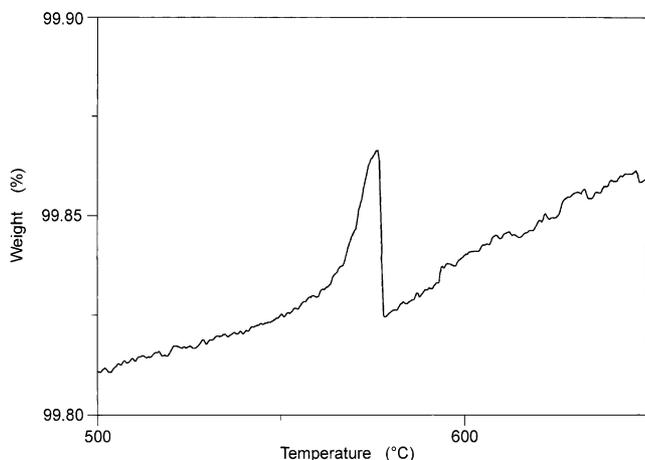


Fig. 4. TGA curve of magnetite microcrystals.

that this habit prevails after their decomposition, to give as final product magnetite, as was already discussed in the precedent paragraph. Thus the unusual prismatic habit for magnetite is probably due to the heterogeneous nucleation of magnetite on iron oxalates.

Fig. 6a is a photograph of a magnetite microcrystal observed between crossed polarizers in transmitted light. Magnetic domains are visible due to the Faraday effect [19]. All the observed microcrystals were multidomains stripe-like, with domain walls oriented almost parallel to the major edge of the crystal, namely, [111] direction, the easy magnetization direction. On applying a magnetic field parallel to the edges, it was possible to observe that some domains become curl, as can be seen in Fig. 6b. Domain pattern is determined strongly by the orientation of the surfaces with respect to the easy directions and the dimensions of the samples. A detailed analysis of these micromagnetic structure is under progress. These magnetite microcrystals were used to prepare a MR fluid by dispersing the crystals in silicon oil. Under an applied magnetic field, the crystals form clusters that can be characterized by its fractal dimension. Experimental studies concerning sound

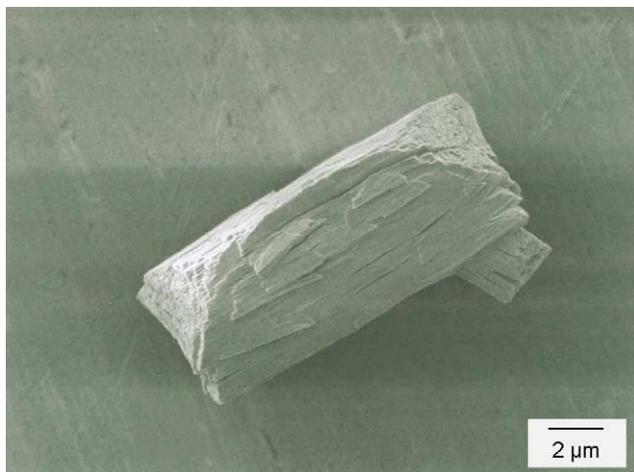


Fig. 5. SEM photograph of an elongated prismatic magnetite crystal.

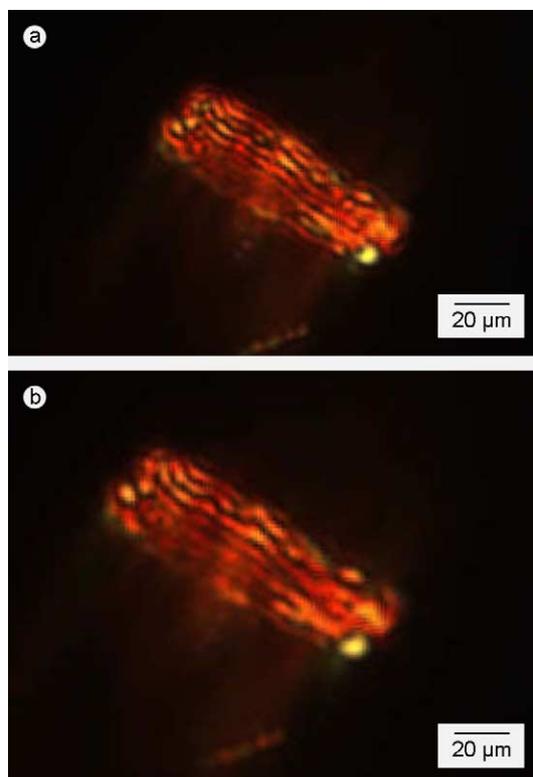


Fig. 6. PLM photograph of magnetic domains in magnetite as observed (a) without magnetic field, (b) with magnetic field applied parallel to the major edges.

propagation in this MR fluid have been successfully explained considering the cluster structure formed by microcrystals [20,21].

Elongated prismatic microcrystals of magnetite were prepared by a new chemical coprecipitation reaction. Crystal habit and size of crystals were homogeneous, stripe magnetic domains were observed by means of Faraday effect, domain walls were oriented parallel to [111].

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