

Nanocrystalline/nanosized Fe_3O_4 powder obtained by mechanosynthesis

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Keywords: nanocrystalline/nanosized material, magnetite, mechanical milling, magnetic material.

Abstract. Nanocrystalline/nanosized magnetite - Fe_3O_4 powder was obtained by mechanical milling of well crystallized magnetite obtained by ceramic method starting from stoichiometric mixture of commercial hematite - Fe_2O_3 and iron - Fe powders. The mean crystallites size of the magnetite is decreasing upon increasing the milling time down to 6 nm after 240 minutes of milling. After 30 minutes of milling an undesired hematite phase is formed in the material. The amount of this phase increases upon increasing the milling time. In the early stage of milling (up to 30 minutes) the existence of nanometric particles (mean size below 100 nm) is noticed. The d_{50} median diameter decreases first (up to 5 minutes of milling) and after that, an increase follows for milling times up to 120 minutes. Saturation magnetization decreases upon increasing the milling time and is more difficult to saturate. X-ray diffraction, laser particle size analysis and magnetic measurements have been used for powder characterization.

Introduction

The soft magnetic ferrites represent a large class of magnetic materials that are used in various fields from to electronic industry to medical applications. The general chemical formula for the soft magnetic ferrites is MeFe_2O_4 where Me is a metallic cations (Ni, Fe, Cu, etc) or a group of metallic cations with a total valence of 2+. These soft ferrites have the characteristic cubic spinel structure and are exhibiting a ferrimagnetic ordering. The cubic spinel structure characteristic for the ferrites allows two types of sites for the metallic cations: tetrahedral (A) and octahedral (B) [1-3]. Among the soft ferrites materials one of the most interesting is iron ferrite, Fe_3O_4 (FeFe_2O_4), also known as magnetite (iron ferrous ferric oxide). Magnetite has a cubic inverse spinel structure where the iron cations (Fe^{2+} and Fe^{3+}) are occupying both tetrahedral and octahedral sites. The magnetite has a magnetization of 4 μB /molecule and an electrical resistivity of $4 \cdot 10^{-3} \Omega \cdot \text{cm}$ [1, 2]. As it is well known the materials in nanocrystalline/nanosized state have in general modified characteristics as compared to the well crystallized counterparts [1, 3]. The mechanosynthesis is one of the suitable methods used for the synthesis of the nanocrystalline/nanosized soft magnetic ferrites. It has been used for the obtaining of several types of soft magnetic ferrites: ZnFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , MnFe_2O_4 , etc [4-9]. The synthesis of the magnetite in nanocrystalline/nanosized state enlarged his range of applications. Therefore, the iron ferrite special characteristics offered by nanocrystalline/nanosized state make this material suitable for applications such as: magnetic storage devices, mineral separation, catalysis, magnetic refrigeration system, hyperthermia, immunoassay, drug delivery, magnetic resonance imaging, cancer therapy or magnetic cell separation [10-14]. In this work we will concentrate on the synthesis, structural and magnetic characterization of nanocrystalline/nanosized magnetite powder.

Experimental

The Fe_3O_4 has been synthesized by ceramic method starting from stoichiometric mixture of commercial hematite - Fe_2O_3 (Alpha Aesar) and iron - Fe (Höganäs) powders. The stoichiometric mixture of Fe_2O_3 and Fe has been homogenized in a turbula type apparatus for 15 minutes. The iron and hematite homogenized mixture has been heat treated in argon at the temperature of 600 °C for 10 hours in a tubular furnace. After the heat treatment, the samples have been mechanically milled for up to 240 minutes in a high energy planetary ball mill (Fritsch, Pulverisette 6). For the ball milling process, a vial of 250 ml and balls with the diameter of 14 mm have been used. A rotational speed of 350 rpm and a ball to powder ratio of 20:1 were set. The X-ray diffraction patterns were recorded by a Siemens D5000 diffractometer which operates in reflection with CoK radiation. The diffraction patterns have been recorded in an angular range of $2\theta = 20\text{-}100^\circ$. The mean crystallites size was calculated by X'Pert HighScore software. A Laser Particle Size Analyzer (Fritsch Analysette 22-Nanotec) with an analysis field of 10 nm to 2000 μm was used for particles size distribution and d_n parameters determinations. The $M(H)$ curves were recorded at room temperature (300 K) using the extraction sample method in a continuous magnetic field of up to 10 T.

Results and discussion

The X-ray diffraction patterns of the Fe_3O_4 samples mechanical milled for 1, 3, 5, 15, 30, 60, 120, 180 and 240 minutes are compared in Fig. 1 to the corresponding pattern of Fe_3O_4 sample produced by conventional ceramic route. By such ceramic method Fe_3O_4 is obtained using Fe_2O_3 and Fe as precursors. In the diffraction pattern of the ceramic sample the peaks of the iron ferrite-magnetite cubic spinel structure can be easily observed. Also, it can be noticed that, the ferrite is not 100 % pure. Indeed, after the heat treatment noticeable amounts of FeO - wüstite and Fe are present in the obtained material. It can be observed in the diffraction patterns of the mechanically milled samples that the diffraction peaks becomes broader and broader by increasing the milling time as compared to the peaks of the well crystallized ceramic sample. This indicates the reduction of the magnetite crystallite size and it is typical for the mechanical milling process. Upon increasing the milling time, the diffraction peaks of the main phase (magnetite) become more broadened as compared to the diffraction maximum of the residual Fe phase. This is assigned to the more fragile cubic spinel structure of the ferrite as compared to the ductile structure of iron, which leads to a rapid decrease of the crystallite sizes. One can also notice that after 30 minutes of milling the peaks characteristic for hematite iron oxide – Fe_2O_3 are visible in the diffraction patterns. The occurrence of this oxide can be attributed to some oxidation of the powder during milling process.

The mechanical milling process leads to the decrease of the mean crystallite size of the iron ferrite as we have mentioned above. The reduction of the crystallites takes place progressively as can be observed in Fig. 2 presenting the evolution of the mean crystallite size as a function of mechanical milling time. The mean crystallite size was calculated by the analyses of X-ray diffraction peaks. In the first 30 minutes of milling it can be noticed that a drastic decrease of the crystallites size occurs. After that, upon increasing the milling time up to 240 minutes, a small decrease of the mean crystallite size occurs. At the end of the milling process, after 240 minutes of milling, the mean crystallites size of the magnetite powder is about 6-7 nm. Such a decrease of the mean crystallites size is typical in the case of mechanical milling materials [7, 15].

In the Fig. 3 are presented the particles size distributions obtained by laser particle size analysis for the Fe_2O_3 and Fe precursors samples, Fe_3O_4 ceramic sample and Fe_3O_4 mechanically milled samples for 1, 3, 5, 15, 30, 60, 120, 180 and 240 minutes. The hematite precursor powder has fine particles, less than 4 μm . The iron particles are less than 100 μm that is much larger as compared with the ones of hematite. The magnetite ceramic sample has a multimodal distribution. This is somehow expected since the starting mixture is composed by a combination of fine and large particles. In the first minutes of milling a tendency of particles size reduction is observed. After 3

minutes of milling it can be noticed that a part of the particles have less than 100 nm in diameter. Similar distribution can be noticed for the sample milled for 5 minutes. For milling times longer than 5 minutes the particle size increase and up to 30 minutes of milling the particles with the diameter lower than 100 nm are present as can be observed, the particles size distribution ends suddenly. This comes to confirm that the magnetite powder beside its nanocrystalline state has nanosized particles and so, the powder is in nanocrystalline/nanosized state. For prolonged milling times (180 and 240 minutes) of milling the particles dimension tends to become uniform and the particles distribution is bimodal, within the 0.1 – 70 μm range. In the case of the samples milled for milling times longer than 30 minutes it can be assumed that the nanometric particles are present. These particles are probably attached one to another or to larger particles and during measurements when are subjected to ultrasonic bath the separation is not accomplished.

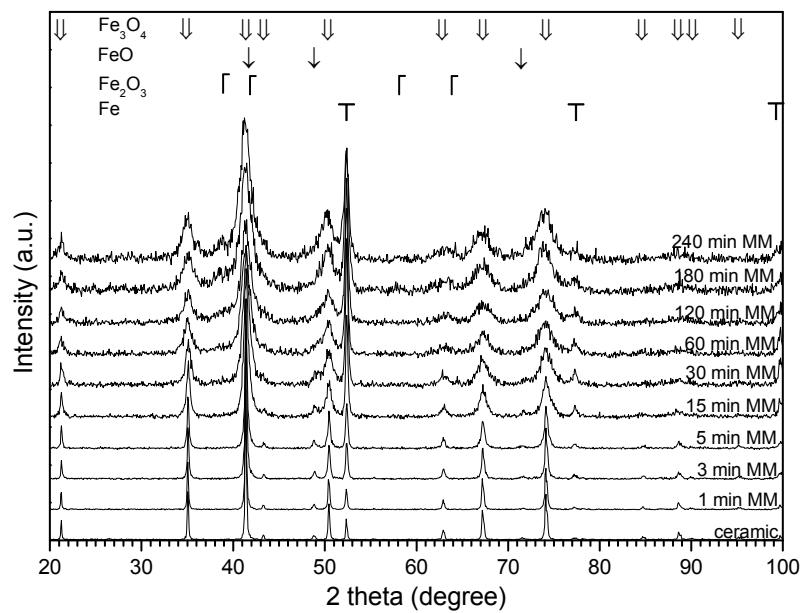


Fig. 1. X-ray diffraction pattern of the Fe_3O_4 sample produced by ceramic route compared to that of Fe_3O_4 samples mechanically milled for 1, 3, 5, 15, 30, 60, 120, 180 and 240 minutes.

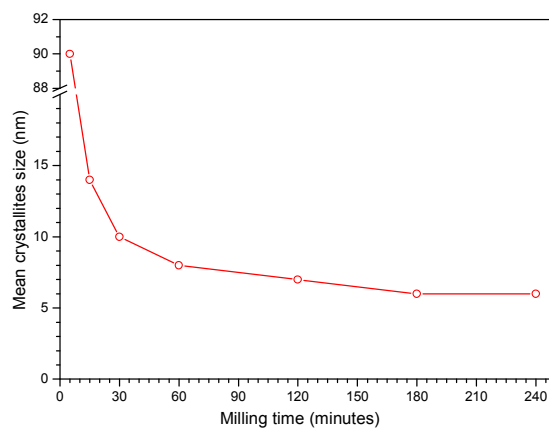


Fig. 2. Evolution of the mean size of magnetite crystallites versus milling time.

In the Fig. 4 is presented the evolution of the d_{50} median diameter of the magnetite particles as a function of milling time. In the first minutes of milling the particles mean diameter is reduced down to less than 2 μm . This fact is assigned to the predominance of the fragmentation process in the early stage of milling [15]. The decrease of the particles is followed by a significant increase up to 120 minutes of milling. The mean diameter of the powder particles is at about 5 μm . During this period of milling it is presumed that the welding process becomes predominate instead of the fragmentation ones.

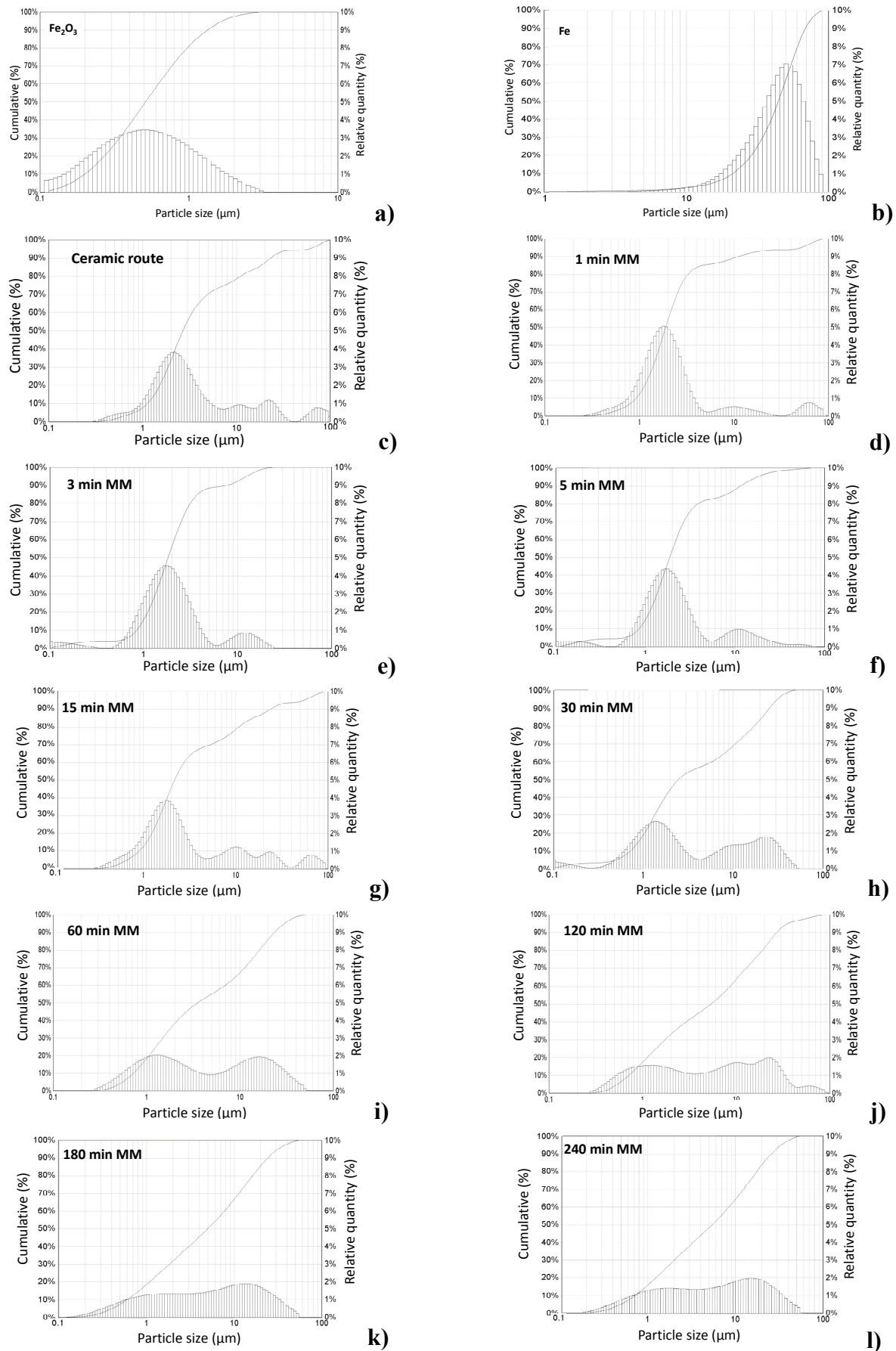


Fig. 3. Particle size distributions obtained by laser particle size analysis of: **a)** and **b)** Fe_2O_3 and Fe precursors, **c)** Fe_3O_4 ceramic sample and **d), e), f), g), h), i), j), k), l), m)** Fe_3O_4 mechanically milled samples for 1, 3, 5, 15, 30, 60, 120, 180 and 240 minutes.

After 120 minutes of milling, equilibrium among fragmentation and cold welding processes seems to take place since the mean diameter of the particles is preserved at almost the same value, around 5 μm . This equilibrium among fragmentation and welding processes explain the bimodal/quasi-bimodal particles size distribution observed for the major part of these samples.

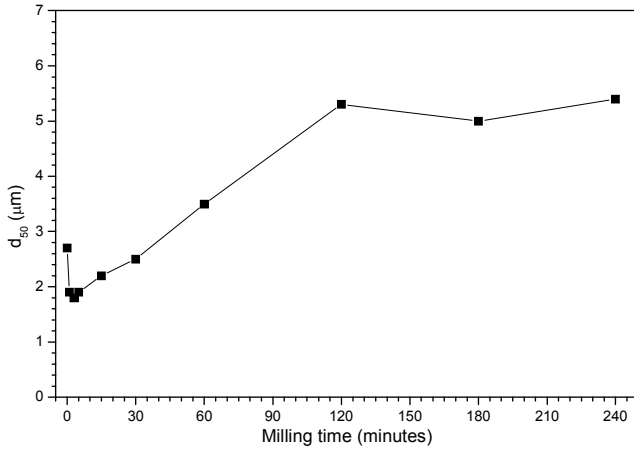


Fig. 4. Evolution of the d_{50} median diameter of the magnetite particles versus milling time.

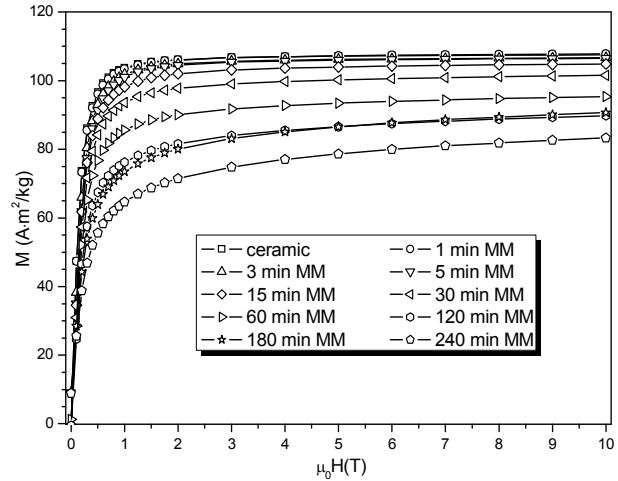


Fig. 5. Room temperature first magnetization curves of the un-milled and milled magnetite samples.

In the Fig. 5 are presented the room temperature magnetization curves of the Fe_3O_4 ceramic sample and Fe_3O_4 samples mechanical milled for 1, 3, 5, 15, 30, 60, 120, 180 and 240 minutes. The magnetization samples milled for very short periods (up to 5 minutes) remain at almost the same values as for the ceramic sample. This suggests that the mechanical milling process does not lead to a significant change of the magnetic structure for such short period of milling. Further increase of the milling time leads to a decrease of the magnetization. The decrease is moderate up to 30 minutes of milling and after that a more pronounced decrease can be observed. One can also observe the tendency of the magnetization to become more difficult to saturate even at high external magnetic field. This difficult saturation of the magnetization is due to the spin canted effect that is induced by mechanical milling process. The spontaneous magnetization decrease on the one hand is caused by the existence of particles that have canted spins on the surface and, on the other hand by the structural disorder and defects that are induced in the material by mechanical milling [3-6]. For the samples whose X-ray diffraction exhibits also a hematite phase, the decrease of the magnetization is caused by the presence of this extra phase. Indeed a transformation of the magnetite into nonmagnetic hematite or the oxidation of magnetite or of the undesired Fe phase could all lead to the magnetization decrease.

Summary

The nanocrystalline/nanosized Fe_3O_4 was successfully obtained by mechanosynthesis of the well crystallized magnetite powder produced by ceramic method. The starting sample of magnetite has been obtained by ceramic route by reaction of stoichiometric mixture of hematite and iron. The mean crystallites size of the magnetite is progressively reduced upon increasing the milling time up to 240 minutes. After 240 minutes of mechanical milling, the mean crystallites size of the magnetite is at 6 nm. In the first minutes of milling, up to 30 minutes, the powder consists in nanometric particles (below 100 nm) and nanocrystalline micrometric particles. The d_{50} particles mean diameter decreases in the first stages of the mechanical milling process and after that a significant increase is noticed up to 120 minutes of milling, followed by a relative stabilization within the studied period (of) up to 240 minutes. Saturation magnetization of the nanocrystalline ferrite is lower as compared

to the well crystallized counterpart due to the existence of the spin canted, structural disorder and defects induced by the mechanical milling process.

Acknowledgement

This paper was supported by the Post-Doctoral Programme POSDRU/159/1.5/S/137516, project co-funded from European Social Fund through the Human Resources Sectorial Operational Program 2007-2013.

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