

Magnetic Properties and Sorption Activity of Mechanically Activated Magnetite Fe_3O_4

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It is known that the action of mechanical forces on solids (mechanical activation and/or mechanochemistry) leads to changes of their properties and reactivity. We have studied the physico-chemical and sorption properties of magnetite Fe_3O_4 (Kiruna, Sweden) mechanically activated in a planetary mill. Several methods such as X-ray diffractometry, Mössbauer spectroscopy, magnetometry, specific surface area measurement as well as arsenic sorption tests have been applied. By X-ray diffractometry strong amorphisation of magnetite has been evidenced. In parallel, specific surface area increased from $0.1 \text{ m}^2/\text{g}$ for the reference (non-milled) sample to the values $0.5\text{--}6.1 \text{ m}^2/\text{g}$ for milled samples. The Mössbauer spectrum of the reference sample is well fitted with two subspectra corresponding to tetrahedrally (A) and octahedrally (B) coordinated iron cations in the spinel structure of Fe_3O_4 . In mechanically activated samples (B)-site subspectrum becomes asymmetric, while (A)-site spectrum remains more or less unchanged. The more covalent character of the Fe(A)–O bond compared to the Fe(B)–O bond can explain qualitatively why the spin-density transfer from (A) to (B) in the spinel structure is more effective than vice versa. The value of the saturation magnetization at room temperature was $67.4 \approx 43.6 \text{ emu/g}$ which is significantly lower than that of the bulk particles 92 emu/g . This reduction may be attributed to the surface disorder or spin canting at the particle surface. During the milling process the coercivity value increases from 150 Oe up to 460 Oe with milling time. This increase can be related to the fact that magnetic anisotropy may increase when particle size decreases. The sorption activity of Fe_3O_4 was enhanced as a consequence of its disordering: 88% of As^{3+} was captured for the mechanically activated sample in comparison with 0% for the non-milled one.

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1. Introduction

There is a considerable interest in magnetite in connection with its ubiquitous occurrence in nature and advanced applications. For example, the mineral magnetism is primary concerned with its occurrence on Earth and Mars and link to past life on the planets [1] and its presence in living organisms [2]. The advanced applications include its utilization in magnetic fluids injected into tumor issue (“dextran-magnetites”) in order to apply them at hyperthermia treatment of cancer [3], magnetic targeting [4] and last but not least magnetite environmental potential for arsenic uptake [5–7]. Magnetite Fe_3O_4 with its spinel structure $(\text{Fe(III)})[\text{Fe(II)Fe(III)}]\text{O}_4$ has tetrahedrally (A) and octahedrally (B) coordinated iron cations and strong ferrimagnetism. In fact, the

structure of magnetite is that of an inverse spinel, that is one-third of the iron as Fe(III) occupies all the available A sites, one-third as Fe(III) occupies half of the B sites, and one-third as Fe(II) occupies the other B sites [8]. This inner structure can be modified by external action, e.g. by thermal or mechanical effects. Mechanochemistry [9–14] with its potential to create metastable states in solids by milling seemed to be proper tool for such intervention.

It is aim of this paper to study the structural, magnetic and surface properties as well as the sorption ability of magnetite Fe_3O_4 modified by high-energy milling.

2. Experimental

The investigation was carried out with mineral magnetite (Kiruna, Sweden). Only magnetite Fe_3O_4 (JCPDS 19-0629) and a small amounts of quartz SiO_2

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(JCPDS 46–1045) were determined by X-ray diffractometry (XRD) in the sample. The high-energy milling was performed in a planetary mill Pulverisette 6 (Fritsch, Germany) under the following conditions: loading of the mill with 50 balls (10 mm diameter), material of milling vial and balls: tungsten carbide; ball charge 360 g; weight charge of sample 5 g; rotation speed of the mill 500 rpm; milling times 5–60 min. The XRD measurements were performed by employing the X-ray diffractometer X'Pert SW Philips. The Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$) was used at 40 kV and 50 mA generation settings. The scan step time was 40 s at step size 0.033° (2θ). The degree of magnetite amorphization was calculated by method published in [14, 15]. The samples were left uncovered from any conductive material in order to keep their original properties. The specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus Micromeritics. The Mössbauer spectra were taken in transmission geometry at temperature 293 K. A $^{57}\text{Co/Rh}$ γ -ray source was used. The velocity scale was calibrated relative to ^{57}Fe in Rh. Recoil spectra analysis software with Voigt-based fitting method [16] was used for the quantitative evaluation of the spectra. The magnetic properties of the prepared samples were carried out by SQUID magnetometer of Quantum Design at room temperature. The coercive force was estimated from hysteresis measurements.

The sorption tests were performed with initial As concentration 5 mg/L prepared from NaAsO_2 . The sorption was running in Erlenmeyer's banks placed on a laboratory shaker. The sampling was made till 6 h and residual concentration of As in solution was determined by atomic absorption spectroscopy method (SPECTRAA L40FS/L40Z, Varian, Australia).

3. Results and discussion

It has been established that during mechanical activation no new phases were formed as a possible consequence of magnetite \rightarrow hematite transformation. This phenomenon has been observed in literature by milling till 100 h [17]. In this case a highly dispersed hematite was identified as the end product of mechanochemical activation. However, strong XRD amorphization (80–90%) in our samples together with an increase of specific surface area (from $0.1 \text{ m}^2/\text{g}$ to $6.1 \text{ m}^2/\text{g}$) were evidenced in our samples.

The Mössbauer spectrum of the reference sample (Fig. 1 α) is well fitted with two subspectra (light and dark grey) corresponding to tetrahedrally (A) and octahedrally (B) coordinated iron cations in the spinel structure of Fe_3O_4 [8]. In mechanically activated sample (B)-site subspectrum becomes asymmetric, while (A)-site subspectrum remains more or less unchanged (Fig. 1 β). The more covalent character of the Fe(A)–O bond compared to the Fe(B)–O bond can explain qualitatively why the spin-density transfer from (A)- to (B)-sites in the spinel structure is more effective than vice versa.

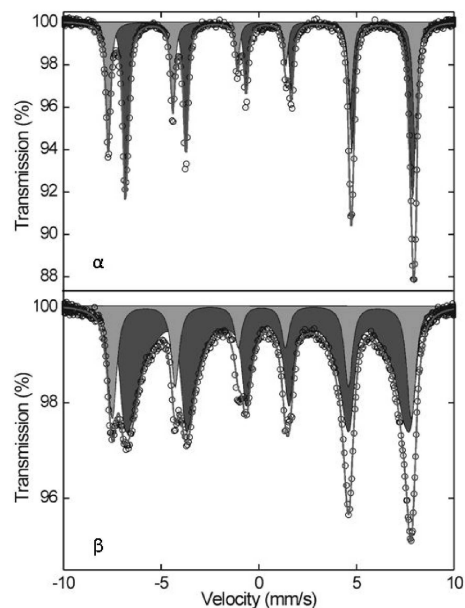


Fig. 1. Room-temperature Mössbauer spectra of Fe_3O_4 . Mechanical activation: α — 0 min, β — 60 min, light grey — tetrahedrally, dark grey — octahedrally coordinated iron cations.

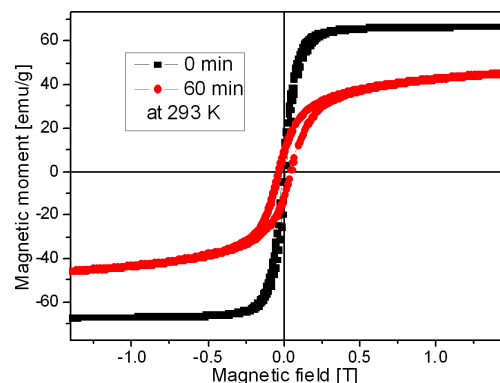


Fig. 2. Room temperature hysteresis loops of mechanically activated Fe_3O_4 for 0 min and 60 min, respectively.

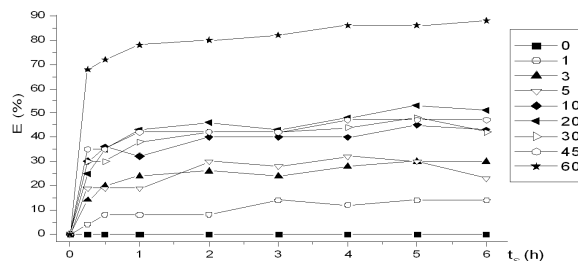


Fig. 3. Removal efficiency of arsenic, E , vs. sorption time, t_s , for Fe_3O_4 . Mechanical activation 0–60 min.

The magnetization curves of samples without milling and with 60 min milling are shown in Fig. 2. The saturation magnetization of sample without milling is 67.4 emu/g and coercive force is 150 Oe. After milling of 60 min, the saturation magnetization is decreased to 43.6 emu/g and the coercive force increased to 460 Oe. The value of the saturation magnetization at room temperature is significantly lower than that of the bulk magnetic particles 92 emu/g. This reduction may be attributed to the surface disorder or spin canting at the particle surface. On the other hand, the coercivity after 60 min milling is more than twice larger than that of initial Fe₃O₄. We consider that the enhanced H_c may result from the increase of the magnetic anisotropy as a consequence of particle size decrease during the milling process. Existence of the oxide layer on surface of magnetite particles coupling between core and shell in particle may be another reason for increasing coercivity [18].

The results of removal efficiency of arsenic by mechanically activated magnetite particles for 0–60 min are given in Fig. 3. Milling markedly influences As sorption as a consequence of specific surface area increase as well as bulk changes induced in mineral. The increase of As capture is especially enhanced for milling time 60 min. This jump is surely in close relation to the specific surface area increase at these milling times as well as bulk disordering. For example, for sample milled for 60 min only 12% of the non-sorbed arsenic was detected in solution. For comparison, non-treated magnetite has no potential for arsenic uptake. Environmental aspects of this phenomenon are obvious.

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