

Structural and magnetic domains characterization of magnetite nanoparticles

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Abstract

Recently, important advances have been achieved in application, reproducibility and response ability of magnetic materials due to the relationships among processing, structure and nanometric size particle. Features like homogeneity of compounds and nanoparticle-sizing have improved some magnetic properties of materials and their field application. Of particular interest is the study of magnetic materials at the atomic and microstructural level because the orientation and magnetic domains (large numbers of atoms moments coupled together in a preferential direction) can be observed. In this work, magnetite (Fe_3O_4) powders which were obtained by precipitation route in alkaline medium are analyzed to identify the structure and mechanism formation of domains over the core and border of nanoparticles. Results obtained by XRD, atomic force microscopy (AFM) and magnetic force microscopy (MFM) showed a structural phase corresponding to Fe_3O_4 and nanoparticles in a range of 20–40 nm. Samples scanned by MFM in nanometric resolution and profile images showed orientation of magnetic domains in the border and cores of the material. Finally, an analysis of repulsion and attraction in magnetic field and direction changes of domains formed by magnetite (Fe_3O_4) powders were done.

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1. Introduction

The research and analysis of effects in magnetic nanostructured materials has enabled the improvement of the study of the magnetic properties of magnetite, Fe_3O_4 [1]. The great interest in these materials is determined by the possibilities for different applications in electronics (magnetic ink, recording media) and medicine (magnetic resonance contrast media or therapeutic agents in cancer treatment, etc.). Each application requires different material properties—thermal, chemical, colloidal stability, magnetic characteristics, particle shape and size, or non-toxicity [2]. Fe_3O_4 ferromagnetic nanoparticles have a strong influence on the magnetic behavior of these magnetic nanostructured materials therefore the formation of monodomains is expected as a result of the small critical size of the magnetic field [3]. The latter characteristic allows the magnetic domains to form a variety of patterns with different orientations depending on the magnetic anisotropies and positions of nanoparticles. Usually, in the said materials, two main regions are analysed: the core as well

as the border of nanoparticles. When in plane anisotropy is present together with a perpendicular one, a creation of an ordered system of quasi-parallel stripes may be expected [4,5] since all of the atomic dipoles are coupled together in a preferential direction in each domain.

Recent advances in magnetic nanostructured materials have been done by characterization of magnetic domains in nanoparticles surface with magnetic force microscopy (MFM), detecting the stray field in magnetic samples [6–9]. Studies on MFM have been focused essentially on magnetic recording media and multidomain magnetic materials as well as on tip characterization and complemented with topography analysis by atomic force microscopy (AFM) [10]. MFM images are formed by scanning the attractive and repulsive magnetostatic field with the interactions between the shape of the magnetic tip in vertical direction and the surface of a sample in horizontal position. If magnetization of the sample is oriented along the vertical direction (z -axis) and the tip can be represented as a magnetic dipole with magnetization along the z -axis; the shifts are represented on MFM images by dark and bright regions, where the field is formed. So, large negative shifts (repulsion) are dark whilst large positive shifts (attraction) are bright [11,12].

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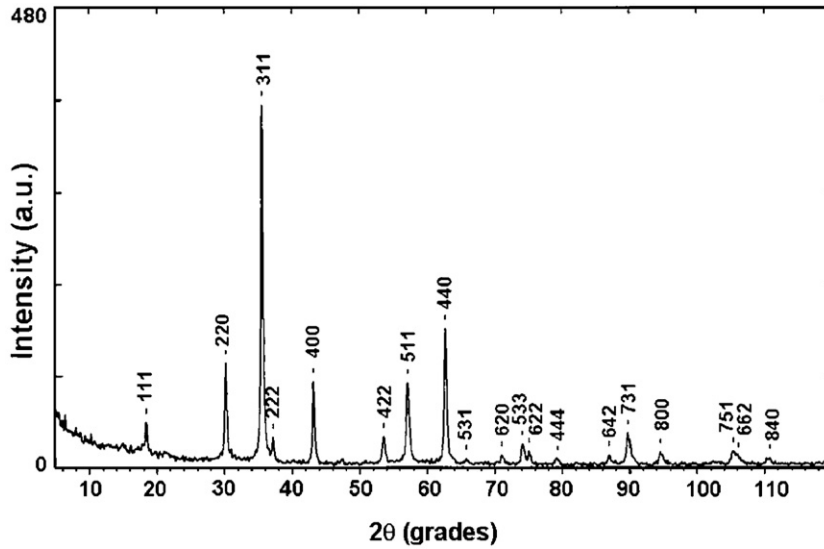


Fig. 1. X-ray diffraction pattern of Fe_3O_4 nanoparticles.

Magnetic anisotropy and coercivity have been observed in small size ferromagnetic particles close to the single domain size. Hence magnetic domains can be ordered in different positions in a polycrystalline material; furthermore, a concentration of domains could present different characteristics in the core and in the nanoparticle boundary [13].

In this paper, an analysis of interactions in the magnetic field is done in order to identify the domain orientations within Fe_3O_4 ferromagnetic nanoparticles.

2. Experimental

Fe_3O_4 nanoparticles were obtained by precipitation route in alkaline medium. Hydrolysis of a 3 M FeCl_2 solution with a 12 N KOH solution whilst stirring for 35 min at 50 °C. Boiling deionized water was added until a black precipitate was formed.

This product was centrifuged and washed with boiling deionized water and dried under vacuum.

Magnetite, Fe_3O_4 , phase identification was carried out with a Siemens-D5000, X-ray diffractometer, with monochromatic $\text{CuK}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$, with 35 kV and 30 mA. Scanning steps of 0.01, 2θ degrees were used in the range 5–120°, with 3 s/step. For accurate determination of lattice parameters a Data Base Powder Diffraction File, JCPDSPDF, release 2004, International Center for Diffraction Data, ICCD was used.

Fe_3O_4 nanoparticles were confined in a copper adhesive tape in order to scan their surface. Topography was scanned by AFM with a Scanning Probe Microscope (SPM), JEOL JSPM-4212, in Tapping™ mode under normal pressure conditions. Magnetic tip NSC14/Co–Cr, Mikro-masch Co. was used with resonant frequency of 160 kHz, at different RMS conditions. Domains were observed in lift mode, MFM with interaction in height of

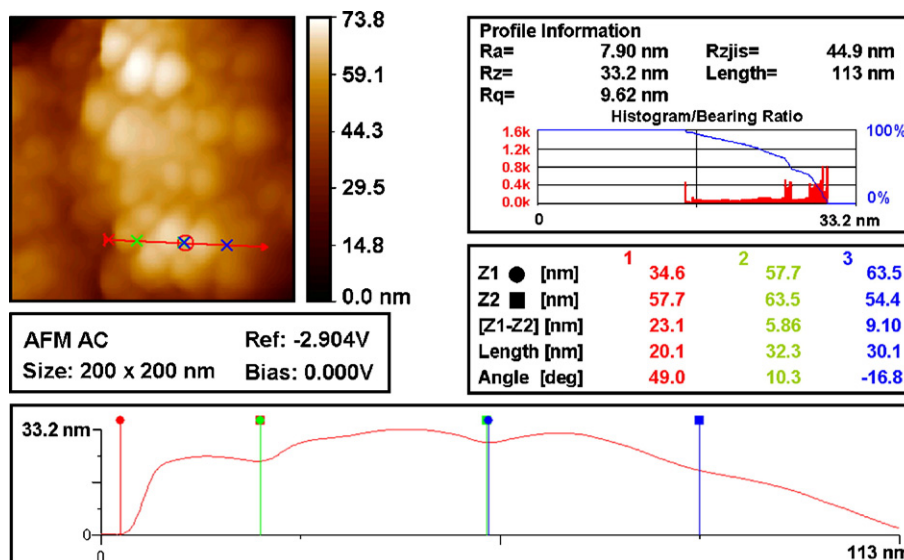


Fig. 2. 2D image and profile in transversal direction across Fe_3O_4 nanoparticles.

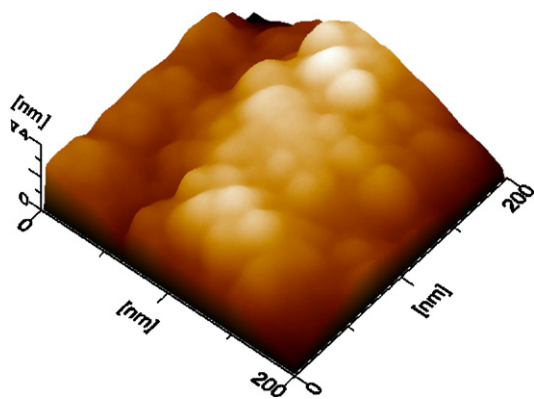


Fig. 3. 3D image of Fe_3O_4 nanoparticles.

25 and output of 0.025 A/V. The 3D images, profiles, and domains measurements were processed with winSPM DPS version 2.0, software JEOL Ltd.

3. Results and discussion

3.1. Structural analysis by XRD

The XRD powder pattern showed a crystalline material which was identified as pure magnetite Fe_3O_4 phase with cubic structure, $a=8.396 \text{ \AA}$ and special group $Fd\bar{3}m$ (227), PDF: 19–629, Fig. 1. The width of the peaks indicates the presence of small particles of nanometric size. Complementary analysis by AFM was done in order to confirm the presence of these nanoparticles.

3.2. Topography of Fe_3O_4 nanoparticles

The analysis of magnetic particles consisted in the observation of the surface of Fe_3O_4 nanoparticles. Powders were scanned in an area of $200 \times 200 \text{ nm}$, with a profile measurement nanoparticles were observed distributed in all the area in a range of 25 nm, Fig. 2. In addition, the agglomeration of Fe_3O_4 nanoparticles is evident in the topography image because the powders were confined directly on the copper tape. However, the boundaries and cores are well defined along the

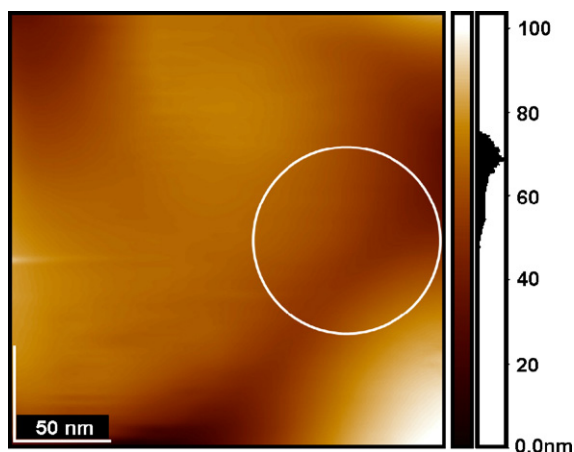


Fig. 4. Border of Fe_3O_4 nanoparticles observed by AFM in Tapping™ mode.

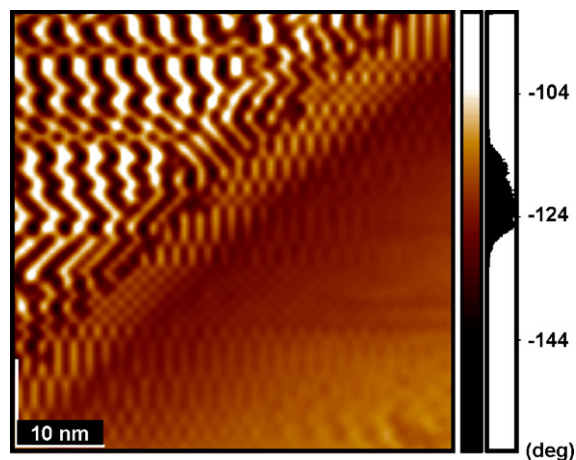


Fig. 5. Domains observed by MFM mode inside the border.

sample as it is shown in 3D image, Fig. 3. For that reason, the distribution and positions of nanoparticles should present anisotropy in the magnetic field formed.

3.3. Magnetic domains in Fe_3O_4 nanoparticles

3.3.1. a) Fe_3O_4 boundary

The first part of the magnetic domains analysis consisted in locating a region near a border in tapping mode in order to appreciate the anisotropy, domains order and preferential directions in a Fe_3O_4 nanoparticle, Fig. 4. In this region, lift mode MFM revealed that all the domains stay in different directions with defined parallel strips due to the anisotropy, direction changes were detected by a zoom inside border, where the strips changed in size and orientation. Well-defined walls and domains shifts were interpreted as negative (repulsion) in dark whilst positive (attraction) in bright regions Fig. 5. Domains formed in the magnetic field were measured in a range of 3–2 nm by the profile following transversal direction across the domains. The width of domains decrease as the field is formed near the border and the change in directions can be influenced by the form, size and position of nanoparticle Fig. 6.

3.3.2. b) Fe_3O_4 cores

Topography of cores of Fe_3O_4 agglomerates observed in Tapping™ mode by AFM can be observed in 3D image, Fig. 7(a). Fe_3O_4 domains of cores are illustrated in Fig. 7(b) where the direction changes are caused by anisotropy. In this image, large domains are shaped in the cores by a saturation of the magnetic field from the cores to the boundaries. The domains interpretation of these is the same as that in the boundary case. A dark zone represents a repulsive force whilst a bright zone is an attractive force. Smaller domains are shaped in the boundaries and anisotropy is observed on these. So the well-defined nanoparticles are essential to define small domains and single domain magnetic cell.

4. Conclusions

A homogeneous Fe_3O_4 compound was obtained by a synthesis precipitation route in alkaline medium which yielded

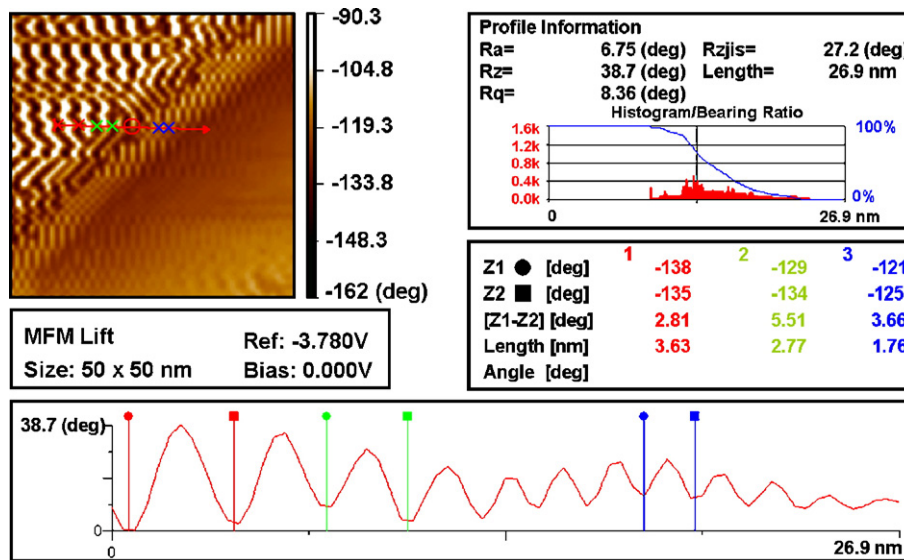


Fig. 6. Fe_3O_4 domains profile inside the border.

nanoparticles in a range of 20 nm. Topography analysed by Tapping™ mode in AFM helped to observe the form and distribution of nanoparticles. Lift mode MFM helped to recognize domains in the core and boundaries, which exhibited patterns of parallel strips in different order, due to anisotropy in the distribution of particles. MFM images showed different zones

where domains formed a parallel sequence following one direction. These domains were in a range of less than ~ 4 nm. A homogeneous distribution of nanometric size particles and shifts in repulsion and attraction of the domains increase the possibility to use these materials in sensors, memories, hard disks and magnetic resonance.

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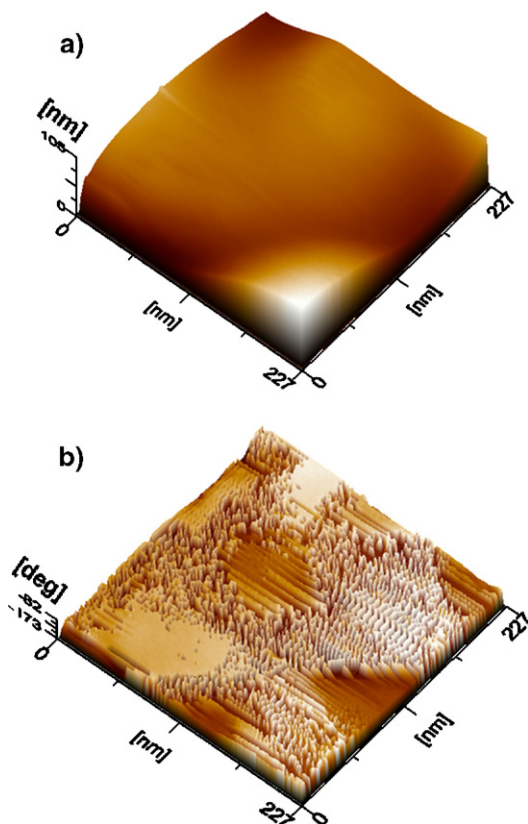


Fig. 7. AFM and MFM analysis in the Fe_3O_4 cores, a) topography and b) domains in the magnetic field.