Monatshefte für Chemie 133, 823–828 (2002)

Monatshefte für Chemie
Chemical Monthly

Microstructure and Magnetic Behaviour of Nanosized Fe_3O_4 Powders and Polycrystalline Films

Ivan Nedkov[1,*], **Toshka Merodiiska**[1], **Svetoslav Kolev**[1],
Kiril Krezhov[2], **Dimitris Niarchos**[3], **Elias Moraitakis**[3],
Yoshihiro Kusano[4], and **Jun Takada**[4]

[1] Institute of Electronics, BAS, BG-1784 Sofia, Bulgaria
[2] Institute for Nuclear Research and Nuclear Energy, BAS, BG-1784 Sofia, Bulgaria
[3] Institute of Materials Science, NCSR 'Demokritos', GR-15310 Athens, Greece
[4] Okayama University, Okayama 700-8530, Japan

Summary. The object of investigation were the magnetic interactions in nanostructured Fe_3O_4 assemblies of two kinds (powder and film) where particles of similar size present nearly uniform domains in a close to planar arrangement with spacings sufficient for magnetic interactions. We discuss the use of the soft-chemistry method, *i.e.* the modified 'ferrite plating' (MFP) technique, for the synthesis of polycrystalline films of magnetite with nanosized crystallites.

Keywords. Magnetite; Magnetic properties; Thin films; Nanostructures; Powders.

Introduction

For nanosized particles, anomalies in the physical properties may be expected; in the case of ferroxide structures they may cause changes in the superexchange magnetic interaction between Fe^{n+} ($n = 2, 3$) cations. One reason for such anomalies is the shape of the nanoparticles. It is known that in nanosized particles the formation of crystalline walls (faces), which is typical for crystals, is unlikely, and their shape is often nearly spherical. The collective magnetic behaviour of nanoscaled crystallites of sizes below the critical diameter for single-domain particles (up to 54 nm for Fe_3O_4 [1]) in the process of their solidification in a polycrystalline film is strongly related to these anomalies and is a subject of current scientific interest. Proposed investigations deal with the magnetic interactions of isolated particles (powders) of nanoscale diameter and thin films of crystallites with a similar diameter, where the intercrystallite spacing is at the limit of fundamental lengths of magnetic interactions.

In the work reported here, the object of studies was magnetite (Fe_3O_4). This compound presents a classical case of a ferrimagnetic spinel-type crystal structure

---

[*] Corresponding author. E-mail: nedkov@ie.bas.bg

and in some sense is a model system [2] for other spinel solid-state solutions. We discuss the use of the modified 'ferrite plating' (MFP) technique for the synthesis of polycrystalline films of Fe_3O_4 with nanosized crystallites. 'Ferrite plating' is a promising chemical method proposed in 1983 by *M. Abe* [3]; it is environmentally friendly and requires neither vacuum nor high temperatures. The modification of the classical technology combines ferrite plating of an aqueous suspension of nanostructured ferrite powders at temperatures of about 100°C with the ferrite coprecipitation processes developed some years ago [4]. MFP makes it possible to obtain polycrystalline thin films under very soft technological conditions, thus allowing for the preservation of the nanosize of the crystallites [5]. We also performed parallel studies on the properties of the basic nanoparticles in the initial suspension and the thin films.

Results and Discussion

The XRD, TEM, and SAED data proved that the deep black coloured powders consisted of a single Fe_3O_4 phase. The *Scherrer* formula applied to the $\langle 311 \rangle$ line and microphotographs were used to select powder samples of different average particle size as a function of aging time. Two kinds of powders with an average grain size of 38 nm ($\pm$20%; **1**) and 6.5 nm ($\pm$20%; **2**) were investigated. Grains with different shapes – spherical, ellipsoidal, and octahedral – were observed in both cases. The spherical grains content was about 80% in **2**, whereas grains with octahedral shape dominated in **1** (*ca.* 85%).

TEM and SAED (Philips CM12 operated at 120 kV) studies of films with a thickness below 1 μm confirmed unambiguously the X-ray diffraction results (Table 1) for single-phase Fe_3O_4 and a near-to-spherical shape of the crystallites with a *quasi*-random orientation and a grain size up to 10 nm (Fig. 1a). For the oxygen content in the Fe_3O_4 film, the SEM (Fig. 1a) and *Rutherford* back-scattering (Fig. 1b) data yielded a ratio Fe:O = 0.73:1 (accuracy: 4%). The slight oxygen excess in the RBS data was estimated to result from overlapping with analytical peaks originating from the SiO_2 substrate.

Figure 2a illustrates the behaviour of magnetization with respect to an applied magnetic field for powders of different particles shape. Nearly no hysteresis losses

Table 1. SAED results for some interplanar distances d_{hkl} of a 1 μm thick Fe_3O_4 film compared with X-ray JCPDS data (file 26-11136)

d_{hkl}/d_{220}	JCPDS	SEAD
111	1.633	1.638
220	1	1
311	0.8528	0.8503
222	0.8164	nor resolved
400	0.7073	0.708
422	0.5773	0.58
511	0.5444	0.547
440	0.5	0.498

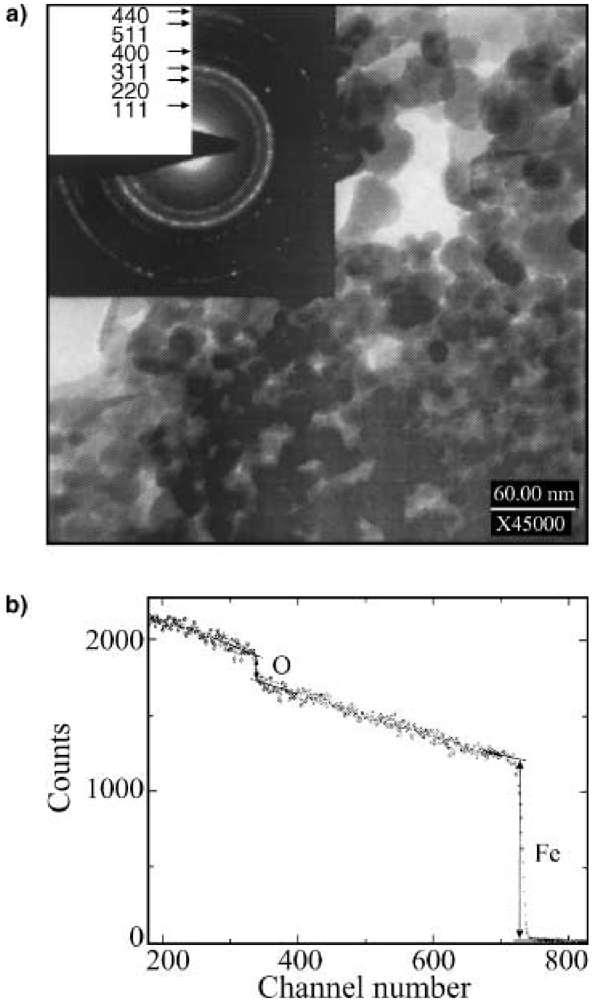

Fig. 1. a) High resolution SEM and SAED; b) *Rutherford* back scattering for the determination of the oxygen and iron content in the Fe_3O_4 thin films deposited by MFP

were observed for the two different powders. The negligible coercive field may be connected with a particle shape different from spherical (shape anisotropy) as well as with the accuracy of the VSM measurements. A considerable difference in the saturation magnetization M_S in both samples was observed. For **2**, a decrease of M_S was detected.

Figure 2b compares sample **2** and the film with 1 μm thickness. The magnetization M_{max} is rather low for the powder, whereas it is near to M_S of bulk material for the film. The hysteresis curve of the polycrystalline sample had a different shape and a slightly higher H_c (of about 150 Oe). However, in both cases of nanostructured materials (powder and film), the field dependence does not indicate clearly a *Verwey* transition.

The neutron diffraction results gave microscopic reasons for the macroscopic decrease of M_S observed for very small size particles. Using the MRIA code, a full profile refinement of the neutron diffraction pattern of a powder sample with a

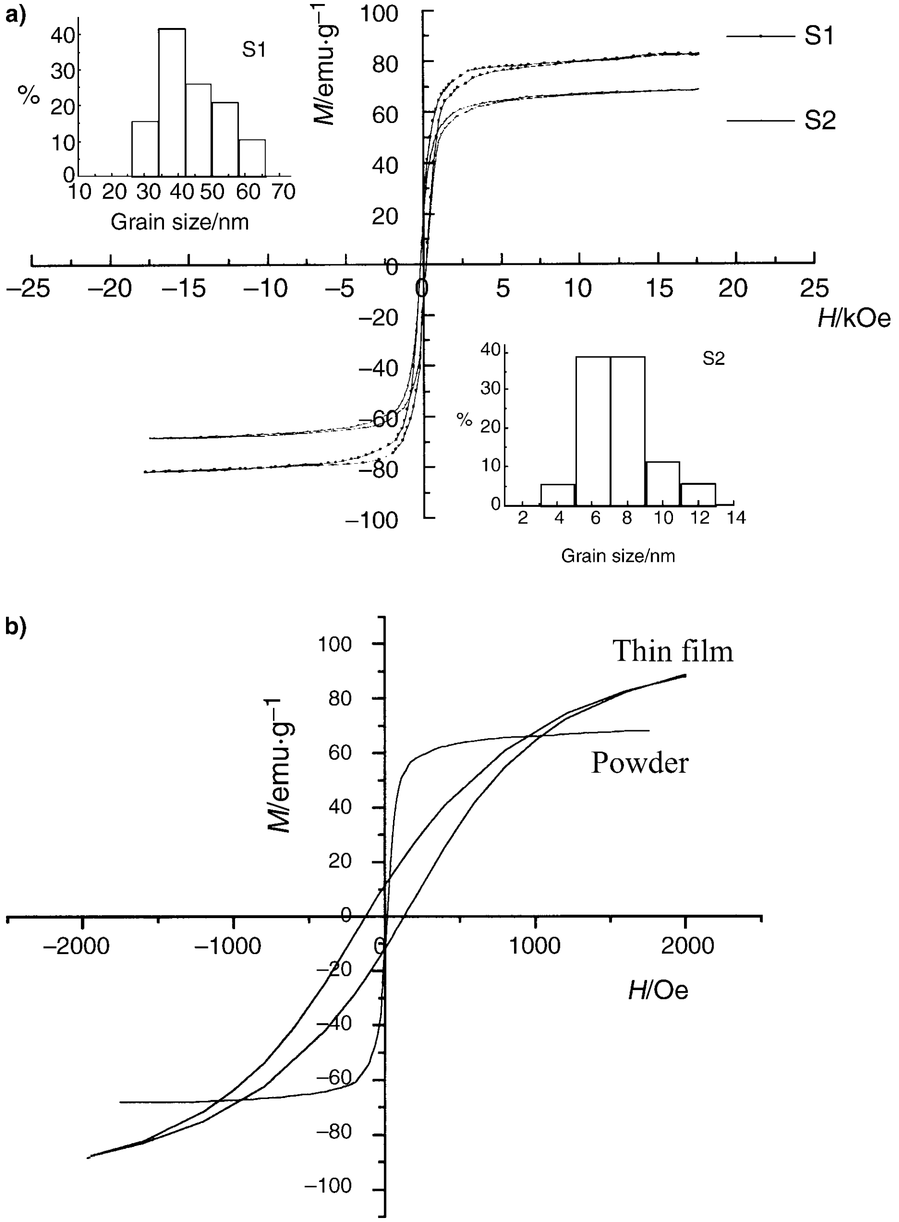

Fig. 2. a) Magnetic losses of Fe_3O_4 powders of different particle size (**1**: average particle size 38 nm; **2**: average particle size 6.5 nm) and b) *M vs. H* curves of polycrystalline films (size of crystallites: about 6.5 nm; spherical shape as obtained by MFP; room temperature)

majority of spherical particles was carried out in space group Fd-3m. Different magnetic structure models were tested. The average grain size was specified in this case as 17 ± 5 nm on the basis of a high-resolution X-ray diffraction pattern taken at room temperature and from the analysis of *Bragg* line broadening by constructing the modified *Williamson-Hall* plot [6]. For the supposed collinear ferrimagnetic structure, the rather low value of $2.6 \pm 0.3\,\mu_B$ resulted for the magnetic moment per formula unit (*M*) from the refined sublattice magnetic moments: $4.1 \pm 0.1\,\mu_B$ per tetrahedral site and $3.4 \pm 0.2\,\mu_B$ per octahedral site. Clearly, the estimated value of M is greatly reduced as compared to the room temperature value of $4.1\,\mu_B$ reported for bulk Fe_3O_4 (see *e.g.* Ref. [7]). Since the interparticle interaction effects are of no relevance for neutron diffraction, the reduction of magnetization reflects intrinsic properties of the particle core related with the Fe^{2+}/Fe^{3+} cationic distribution, local non-collinearity of magnetic moments, or the presence of vacancies. We have to stress at this point that modeling with assumed vacancy ordered or disordered maghemite (γ-Fe_2O_3) yielded diffracted intensity distributions which were inconsistent with the recorded neutron scattering pattern. More experimental details concerning the established dependence of the structural parameters and sublattice magnetic moments on Fe_3O_4 particle size and discussion of the possible sources for this effect have been given elsewhere [5]. It has to be noted that the lattice parameter $a_0 = 8.358(1)$ Å corresponding to this average particle size is significantly lower than that of bulk material. This could be related to the *Laplace* surface superpressure [8], *i.e.* the internal atoms are compressed in the spherical entities forming the nanoparticle assembly. In contrast, as mentioned above, SAED of the films yielded a lattice parameter of $a_0 = 8.395(1)$ Å, perfectly matching the value known for bulk material ($a_0 = 8.396(1)$ Å).

The analysis of the results obtained shows that MFP leads to the deposition of spherical particles only on the substrates, although the initial suspension contains particles with different shape. MFP was carried out at 97°C, and the morphology of the layers thus obtained can be explained by the difference in the dehydration of spherical and octahedral particles. Following the *Young-Laplace* equation for the pressure differential across the interface, the surface of spherical particles creates superpressure, and the internal pressure in the particle is higher than the external pressure. This could give rise to different interactions between the surface of the particle and the surrounding water as compared with the well-shaped orthorhombic particles. The particles present in the suspension with shapes different from spherical are probably ‘washed away’ from the film surface. The adhesion of the spherical Fe_3O_4 particles to the glass substrate is good for layers with thicknesses up to $1\,\mu$m.

Conclusions

The modified ferrite plating (MFP) technique allows the preparation of thin films containing spherical nanosized crystallites with a good adhesion to the substrate due to the dehydration process. In addition, nanostructured thin films and powders of magnetite, although consisting of nanoparticles of similar size prepared by the same technique, exhibit substantially different magnetic and crystallographic properties. The films behave like bulk material, whereas the powder assembly of nanoparticles exhibits a reduced magnetization nearly without hysteresis and a tendency for smaller lattice parameters. The difference in the interparticle interactions reflecting the different size and shape of the particles in the powder assembly as compared with the nearly uniform domains for the close-to-planar arrangement in the films might be the main reason. However, superpressure effects at an interatomic scale resulting in modified superexchange interactions in the single domain powder particles must also be taken into consideration.

Experimental

Wet chemistry was used for powder preparation. The precipitate was formed by addition of NaOH to aqueous solutions of $FeCl_2 \cdot 4H_2O$ and $NaNO_2$ mixed in a strictly fixed ratio. The precipitation process was carried out at $pH = 13$. The resulting deep black coloured substance was filtrated immediately after coprecipitation (**2**) or after aging for 24 h (**1**), washed with distilled H_2O, and dried at 50°C.

The precipitates were used to deposit Fe_3O_4 films on SiO_2 substrates by MFP [4]. The suspensions required for this purpose were prepared from the two kinds of precipitates and distilled H_2O without previous drying. The temperature of deposition was maintained at 97°C. The strongly dispersed precipitate was sprayed on the substrate with the aid of high-purity N_2. The spraying chamber was purged beforehand with N_2 for a long time to avoid oxidation by air. Substrate temperature as well as volume and velocity of the sprayed suspension were chosen to ensure the formation of a layer as uniform as possible. Variation of spraying time and suspension volume afforded layers of different thickness as measured by a *Tallystep* gauge.

X-Ray diffraction (XRD), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED) were applied for phase purity analysis and characterization of the samples. The oxygen content in the Fe_3O_4 films was measured by *Rutherford* back-scattering (RBS) and scanning electron microscopy (SEM). Magnetic measurements on the initial powder and the polycrystalline films were carried out at room temperature using a vibration sample magnetometer (VSM) and a SQUID magnetometer, respectively. Neutron time-of-flight patterns of some of the powders were recorded at room temperature using the DN2 diffractometer of JINR-Dubna.

Acknowledgments

This work was supported by NATO Grant HTECH.L6.973786 and the Bulgarian National Fund for Science (contract F-816). The authors are also indebted to Dr. *L. Milenova* from BAS for her invaluable assistance in organizing some measurements.

References

[1] Aharoni A, Jakubovics JP (1988) IEEE Trans Magn **24**: 1892
[2] Kodama RH, Berkowicz AE (1999) Phys Rev **B59**: 6321
[3] Abe M, Tamaura Y (1983) Jpn J Appl Phys **2**/**22**: L511
[4] Jolivet P, Chaeac C, Prene P, Vayssiers L, Tronc E (1997) J Phys IV France **4**/**7**: C1-537
[5] Nedkov I, Merodiiska T, Koutzarova T (1998) Jpn J Magnetic Society **22**/S1: 378
[6] Somogyvári Z, Sváb E, Mészáros G, Krezhov K, Konstantinov P, Ungár T, Gubicza J (2001) Mat Sci Forum Switzerland **378–381**: 771
[7] Valenzuela R (1994) Magnetic Ceramics. Cambridge University Press, p 321
[8] Klabunde KJ (1994) Free Atom, Clusters, and Nanoscale Particles. Academic Press, San Diego, CA

Received October 22, 2001. Accepted January 21, 2002