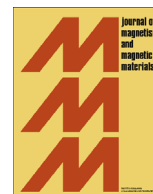




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Alternating magnetic field energy absorption in the dispersion of iron oxide nanoparticles in a viscous medium



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ABSTRACT

Magnetic iron oxide nanoparticles were obtained by a coprecipitation method in a controlled growth process leading to the formation of uniform highly crystalline nanoparticles with average size of 13 nm, which corresponds to the superparamagnetic state. Nanoparticles obtained are a mixture of single-phase nanoparticles of magnetite and maghemite as well as nanoparticles of non-stoichiometric magnetite. The subsequent annealing of nanoparticles at 300 °C in air during 6 h leads to the full transformation to maghemite. It results in reduced value of the saturation magnetization (from 56 emu g⁻¹ to 48 emu g⁻¹) but does not affect the heating ability of nanoparticles. A 2–7 wt% dispersion of as-prepared and annealed nanoparticles in glycerol provides high heating rate in alternating magnetic fields allowed for application in magnetic hyperthermia; however the value of specific loss power does not exceed 30 W g⁻¹. This feature of heat output is explained by the combined effect of magnetic interparticle interactions and the properties of the carrier medium. Nanoparticles coalesce during the synthesis and form aggregates showing ferromagnetic-like behavior with magnetization hysteresis, distinct sextets on Mössbauer spectrum, blocking temperature well about room temperature, which accounts for the higher energy barrier for magnetization reversal. At the same time, low specific heat capacity of glycerol intensifies heat transfer in the magnetic dispersion. However, high viscosity of glycerol limits the specific loss power value, since predominantly the Neel relaxation accounts for the absorption of AC magnetic field energy.

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1. Introduction

Nowadays there are four main concepts of using magnetic iron oxide nanoparticles (NPs), magnetite and maghemite, in medicine: cell separation, imaging, drug delivering, and heating [1–6]. All of these approaches require definite magneto-structural properties of NPs. As an example, there are several commercially available iron oxide formulations for Magnetic Resonance Imaging; however, owing to their superparamagnetic (SPM) behavior and low heating potential in alternating (AC) magnetic fields in a frequency range of hundreds of kHz and amplitudes below 15 kA m⁻¹, they are not suitable for magnetic hyperthermia (MH).

In MH, the ability of a magnetic material (usually a dispersion of magnetic particles in a carrier medium) to dissipate the energy of an AC magnetic field is evaluated by specific loss power (SLP).

There are strict limits on the frequency ($0.05 \leq f \leq 1.5$ MHz) and the amplitude ($H \leq 15$ kA m⁻¹) of the applied AC magnetic field in MH due to physiological restrictions [7]. In this range of field parameters, SLP is defined as [8]

$$\text{SLP} = \pi \mu_0 \chi'' f H^2 / \rho, \quad (1)$$

where μ_0 is the permeability of vacuum, f is the frequency and H is the amplitude of AC magnetic field, χ'' is the imaginary part of susceptibility, and ρ is the mass density of the magnetic material.

Thus, once the parameters of the AC magnetic field are specified for MH, the properties of the magnetic particles must be optimized for the AC magnetic field applied [9,10]. Moreover, it has been shown in [9,11] that the SLP is determined not only by the above-mentioned parameters, but also by the viscosity of the carrier medium.

The total absorption of AC magnetic field energy is determined by two dissipation mechanisms: the intrinsic magnetic dynamics of magnetic moment (Neel relaxation) and the external rotational dynamics of the particle (Brown relaxation) with characteristic Neel

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(τ_N) and Brown (τ_B) relaxation times:

$$\tau_N = \tau_0 \exp(KV/k_B T), \quad (2)$$

$$\tau_B = 3\eta V/k_B T, \quad (3)$$

where τ_0 is pre-exponential factor with the value between 10^{-9} s and 10^{-11} s, K is the anisotropy energy, V is a particle volume, k_B is the Boltzmann constant, T is temperature, ν is the hydrodynamic particle volume, and η is the viscosity of the carrier medium. For a system of magnetic nanoparticles an effective relaxation time, combining the contributions of both Neel and Brown relaxation, characterizes the magnetization:

$$\tau_{\text{eff}} = \frac{\tau_N \tau_B}{(\tau_N + \tau_B)}. \quad (4)$$

An increase in the viscosity of the carrier medium leads to the particles immobilization and increase in τ_B , so that, for $\tau_B \gg \tau_N$, the magnetization occurs only by the Neel mechanism. In [11], it is shown that such a crossover is observed for $\eta \geq 0.1$ P. The vanishing of the Brown relaxation implies a considerable reduction of SLP, and it is common situation taking place when nanoparticles are entrapped in biological medium [12].

The highest reported values of SLP of the order of $1-2$ kW g $^{-1}$ were obtained in a dispersion of iron oxide particles in water [13,14], where two mechanisms of magnetization, Neel and Brown, account for the high heat generation. It should be also noted that these SLP values are obtained for high field amplitudes (much higher than allowed in MH).

The analysis of the relationship between the structural and magnetic properties of the nanoparticles of magnetite and maghemite and their heating efficiency in AC magnetic fields has allowed to identify a set of properties that these particles should have in order to be used in MH: uniformity, phase purity, high crystallinity, a size range corresponding to a stable single-domain state, and high values of saturation magnetization [10,12,15]. Interparticle magnetic interactions are another factor that must be taken into account. Generally, magnetic interactions include both the short-range exchange interaction (under the assumption that the interparticle distance is less than 1 nm) and the long-range anisotropic dipolar interaction. Results on the study of the effect of interparticle interaction on the magnetic properties of a system of nanoparticles and on their heating efficiency in AC magnetic fields are presented in [13,16–21]. These results show both increase and decrease of SLP under the influence of interparticle interactions. Such conflicting information is due to the complex interplay between the factors governing the magnetization process of an ensemble of interacting particles in an external magnetic field: (1) magneto-structural properties of NPs (morphology, saturation magnetization, magnetic anisotropy, etc.), (2) experimental conditions (amplitude and frequency of the AC magnetic field), (3) particles concentration (dosage), and (4) the properties of the carrier medium (viscosity and heat capacity). The analysis of the effect of interparticle magnetic interactions on the integral characteristics of magnetization of a disperse system has shown that the main parameter controlling the heating of nanoparticles is the effective magnetic anisotropy energy, which is determined by the competition between several anisotropies: magnetocrystalline anisotropy, shape anisotropy, surface anisotropy, elastic stress anisotropy, and the anisotropy of interparticle interactions [15].

In a previous work, we have described the coprecipitation reaction course for preparation of iron oxide NPs with reproducible magneto-structural properties adjusted for MH (article submitted to the Journal of Materials Chemistry and Physics). We have shown that, under certain reaction conditions, the rapid nucleation of the magnetic phase followed by slow crystal growth

results in the formation of uniform NPs with average size of 13 nm, polydispersity 0.3, that coalesce into aggregates. The material obtained demonstrates ferromagnetic behavior with magnetization hysteresis. A 2 wt% dispersion of NPs in glycerol shows a high heating rate in AC magnetic fields at different frequencies and amplitudes. These results suggest that the ferromagnetic-like behavior of the material obtained is due to the magnetic interaction between NPs within aggregates. The present study is a continuation of our previous work. The aim of this study is to analyze the effect of magnetic interaction between particles on their collective magnetic properties and the heating efficiency in AC magnetic fields. To this end, we carried out an analysis of the set of structural and magnetic properties of nanoparticles differing in phase composition, as well as the heat efficiency of these particles in AC magnetic fields as a function of their concentration in a viscous dispersion medium.

2. Experimental part

Initial reagents (ferrous and ferric chlorides, ammonium hydroxide, and glycerol) were purchased from Sigma-Aldrich and used without further purification. Demineralized water used for preparing the solutions was deoxygenated by argon bubbling for an hour.

Iron oxide NPs were prepared by coprecipitation of ferrous and ferric salts in an alkaline medium. Solution of ferrous chloride and ferric chloride with a molar ratio of Fe(II)/Fe(III)=0.5 was added dropwise to the excess of ammonium hydroxide solution. The reaction was performed in argon atmosphere at 70 °C under continuous stirring. The black powder of iron oxide NPs formed in the reaction was separated by a permanent magnet, washed with distilled water to neutral pH, and dried in air at room temperature (original sample). Part of dried NPs was annealed at 300 °C for 2 h (2 h annealed sample) and 6 h (6 h annealed sample) in air. All samples were prepared several times to ensure the repeatability of the properties.

The morphology of NPs was investigated using a High Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM-2100F, with a 200 kV field emission). The statistical analysis of the average particle size, d_{TEM} , was carried out on several HRTEM images with different magnification to detect both small and large NPs with the help of Digital Micrograph software (Gatan). For each sample, at least 200 particles were counted. The fast Fourier transform analyses of HRTEM images were performed with the Digital Micrograph software (Gatan) and interpreted using the JEMS software. The crystallographic data for particular iron oxides were taken from the Inorganic Crystal Structure database (ICSD).

The crystal structure and the phase composition of iron oxide NPs were determined by a PANalytical X-Ray powder diffractometer equipped with a PIXcel RTMS detector. The X-Ray diffraction (XRD) data were refined by the Rietveld method using the Fullprof program. The refinement was done using the Fd3m space group for magnetite phase and the P4₁2₁2 space group for maghemite phase. The average crystallite size is determined using Scherrer's formula (incorporated into Rietveld's refinement codes):

$$d_{\text{XRD}} = 0.89\lambda/B \cos \theta, \quad (5)$$

where d_{XRD} is the mean crystallite diameter, λ is the wavelength of X-Ray radiation (CuK α), θ is the diffraction peak angle, and B is the line width at observed half-peak intensity.

The ^{57}Fe transmission Mössbauer spectra (MSs) of samples were recorded using a standard Mössbauer spectrometer in a constant acceleration mode with the ^{57}Co (Rh) gamma-ray source. The isomer shift values were related to α -Fe metal at room

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