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Study on increase in temperature of Co–Ti ferrite nanoparticles for magnetic hyperthermia treatment

Y. Ichiyanagi [a,b,*], D. Shigeoka [a], T. Hiroki [a], T. Mashino [a], S. Kimura [a], A. Tomitaka [a], K. Ueda [a], Y. Takemura [a]

[a] Graduate School of Engineering, Department of Physics, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Japan
[b] Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 3-5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

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ABSTRACT

Co–Ti ferrite ($Co_{1+x}Ti_xFe_{2-2x}O_4$, $0.2 \leq x \leq 0.5$) nanoparticles with average diameters ranging from 6 to 12 nm were produced by a wet chemical method. The imaginary parts of the AC magnetic susceptibility χ'', which is the most dominant value dependent on the thermal energy generated in the magnetic nanoparticles, were measured for samples placed in a 1-Oe, 100-Hz AC magnetic field at room temperature. The temperature corresponding to the peak of χ'' decreased as the value of x increased. The heating mechanisms of the samples were studied on the basis of the dependence of the temperature increase on the magnetic field strength and frequency in the case of the samples with diameters of 12 nm. A temperature increase of approximately 10 K was observed in a 300-Oe, 10-kHz field. The rate of increase in temperature $\Delta T/dt$ was determined to range from 0.001 to 0.008 K/s depending on the frequency and composition. AC magnetic susceptibility measurements revealed that the optimum concentration of Ti ions was found to be that corresponding to $x = 0.3$. These $Co_{1+x}Ti_xFe_{2-2x}O_4$ ($0.2 \leq x \leq 0.5$) samples are expected to be used as thermal agents in magnetic hyperthermia treatment.

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1. Introduction

In recent years, nanoscopic systems have received considerable attention because of their unique magnetic properties as well as their technological applications not only in recording media but also in biomedical engineering. One of the fields in which nanoscopic systems can be employed is magnetic hyperthermia treatment. Hyperthermia treatment is a cancer therapy that involves exposing cancer cells to high temperatures. We expect that a magnetic material will be suitable for use in hyperthermia cancer treatment because this material releases thermal energy upon the application of an external field. Moreover, nanoparticles are sufficiently small to be introduced into cells, and some particles such as magnetite (Fe_3O_4) particles are known to be biocompatible with the human body [1–3].

We have previously reported the magnetic properties of nanoparticles, including those of nanoparticles of transition metals, such as iron oxide nanoparticles [4–6], cobalt oxide nanoparticles [7], and ferrite nanoparticles [8–13] with diameters between 3 nm and 34 nm. It is difficult to maintain the ferromagnetic properties in small-size particles because in a small volume, the magnetic spins fluctuate against thermal energy of k_BT, and an ordered state cannot be maintained [14]. However, we have observed the ferromagnetic behavior of iron oxide nanoparticles with a coercivity of 1 kOe at room temperature, even for particles with diameters as low as 5 nm [4].

In recent several years, the authors have produced functional magnetic nanoparticles (MNPs) in order to realize biomedical applications [15–18]. Magnetic oxides are ceramic insulators; therefore, it is difficult for these materials to attach to any other molecules. Recently, we modified the functional groups, such as the amino, carboxyl, and thiol groups, of MNPs [15–19] and successfully introduced the modified MNPs into cancer cells [18].

In this study, on the basis of the abovementioned technique, SiO_2-shelled Co–Ti ferrite nanoparticles have been developed by a wet chemical method. Further, in this paper, the use of these nanoparticles in hyperthermia treatments has been discussed on the basis of measurements of their AC magnetic susceptibilities. The increase in the temperature of the samples in an AC magnetic field at a specific AC frequency was also measured, and the specific absorption rate (SAR) was evaluated.

2. Heating mechanisms of MNPs

Although it is known that the heating mechanism associated with magnetic hyperthermia is based on both “hysteresis losses”

* Corresponding author at: 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Japan. Tel.: +81 45 339 4185; fax: +81 45 339 4185.
E-mail address: yuko@ynu.ac.jp (Y. Ichiyanagi).

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and "relaxation losses" [19], the theoretical analysis of this heating mechanism is still being carried out. MNPs release heat when they are placed in an AC magnetic field. If the MNPs are placed in an alternative field with a frequency f and amplitude h, the amount of heat A released by the MNPs during one cycle of the magnetic field can be expressed as

$$A = \int_{-h}^{+h} M(H)\ dH, \tag{1}$$

where $M(H)$ represents the magnetization of the particle. Then, the specific absorption rate SAR by hysteresis losses can be expressed as

$$SAR = Af. \tag{2}$$

However, nanoparticles usually exhibit superparamagnetic behavior, and they do not exhibit hysteresis. The energy barrier $\Delta E_B = KV$ depends on the particle volume. Here, energy barrier is the anisotropy energy of the particle, and it is expressed as the product of anisotropy constant K and volume V. If the volume is very small, the thermal energy is higher than the activation energy; as a result, it is easy to induce magnetic spin fluctuations in these particles.

Therefore, in superparamagnetic nanoparticles, the heating mechanism based on relaxation losses is dominant. The magnetic relaxation behavior can be studied by measuring the AC magnetic susceptibility.

The AC magnetic susceptibility χ_{AC} is given by following equation:

$$\chi_{AC} = \chi' - i\chi''. \tag{3}$$

As shown in Eq. (1), χ_{AC} consists of real parts χ' and imaginary parts χ'', where χ' is in phase and χ'' is out of phase with the alternative magnetization. This out-of-phase component contributes to the thermal energy generated inside the MNPs when an AC magnetic field is applied. In our nanoparticle system, the heating mechanism is based on magnetic relaxation losses [19]. Néel relaxation and Brownian relaxation contribute to the magnetic relaxation losses. In the case of Néel relaxation, the magnetic spins in the particle are induced by an alternative field, while in the case of Brownian relaxation, the particles rotate with specific magnetic moments. The Néel relaxation time (τ_N) and Brownian relaxation time (τ_B) are expressed by the following equations [20]:

$$\tau_N = \tau_0\ \exp\frac{KV_M}{k_B T} \tag{4}$$

$$\tau_B = \frac{3\eta V_H}{k_B T}, \tag{5}$$

where K is the anisotropy constant; V_M the volume of the magnetic particle; k_B the Boltzmann constant; T the temperature; η the viscosity of the solvent; and V_H is the hydrodynamic particle volume. Hydrodynamic volume V_H is larger than magnetic volume V_M for surfactant thickness around the particle. Using these relaxation times, the effective relaxation time (τ) can be expressed as

$$\tau = \frac{\tau_B \tau_N}{\tau_B + \tau_N} \tag{6}$$

and power dissipation can be expressed as

$$P = \pi \mu_0 \chi'' f h^2, \tag{7}$$

where μ_0 is the permeability of free space; f the frequency of the applied AC magnetic field; h the strength of the applied AC magnetic field; and χ'' is the imaginary part of the magnetic susceptibility. We can express χ'' as follows:

$$\chi'' = \chi_0 \frac{2\pi\tau f}{1 + (2\pi\tau f)^2}. \tag{8}$$

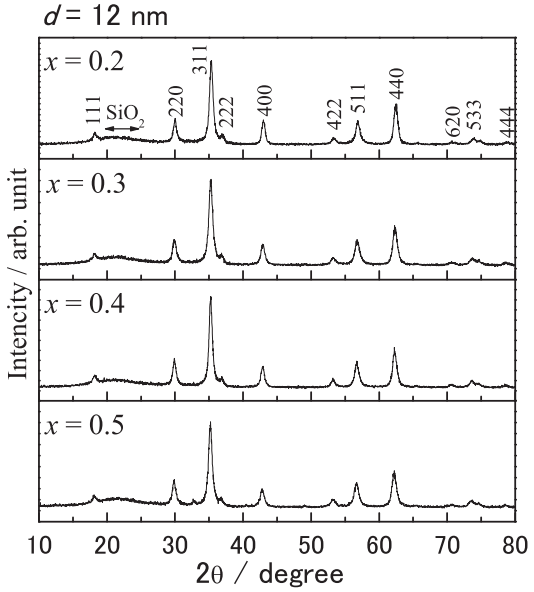

Fig. 1. X-ray powder diffraction patterns for $Co_{1+x}Ti_xFe_{2-2x}O_4$ particles with diameters of 12 nm.

The static susceptibility χ_0 depends on the magnetic field. Thus, χ'' is the most dominant value dependent on the thermal energy generated in the magnetic nanoparticles.

The specific absorption rate (SAR) due to relaxation losses can be expressed as

$$SAR = C\frac{dT}{dt} \tag{9}$$

where C is the heat capacity of the sample and dT/dt is the initial gradient of the temperature increase.

3. Experimental

Co–Ti ferrite ($Co_{1+x}Ti_xFe_{2-2x}O_4$, $0.2 \le x \le 0.5$) MNPs were prepared by a wet chemical method. Solutions of $CoCl_2{\cdot}6H_2O$, aqueous$TiCl_4$, and $FeCl_2{\cdot}4H_2O$ were mixed with a solution of $Na_2SiO_3{\cdot}9H_2O$. The obtained precipitates were dried at 353 K after washing three times; then, the precipitates were annealed at 1173 K in an Ar atmosphere.

The crystalline structure of each sample annealed at various temperatures was observed by X-ray powder diffraction (λ = 0.154 nm). The AC magnetic susceptibilities in an external AC magnetic field were measured using a SQUID magnetometer (Quantum Design, MPMS).

The increase in temperature was measured in an AC magnetic field of 30–500 Oe at a frequency of 50–10 kHz.

4. Results and discussion

4.1. X-ray powder diffraction patterns

Fig. 1 shows the X-ray diffraction patterns for the $Co_{1+x}Ti_xFe_{2-2x}O_4$ (x = 0.2, 0.3, 0.4, and 0.5) samples. From these results, it is concluded that single-phase spinel structures exist in all the different samples. The broad peak observed around 25° corresponds to amorphous SiO_2.

Using the Scherrer formula, the particle diameter was estimated to be about 12 nm on the basis of the half-width of the broad diffraction peaks.

These results are in good agreement with those obtained using a TEM image.

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