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Change in the coercivity of $CoFe_2O_4$ nano-particles verified to result from a change in their domain structure

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Abstract

$CoFe_2O_4$ nano-particles were synthesized using the combustion method. The samples obtained were annealed at different temperatures in order to increase their sizes. Based on the characteristics of the particle size and the magnetic property, a monotonic increase in saturation magnetization from 53.2 to 89.8 emu/g occurred when the particle size increased from 15 nm to >1 μm. However, the coercivity (H_C) did not change monotonically with particle size and it achieved its maximum of 1546 Oe at around 40 nm, which was accompanied by the appearance of a Barkhausen jump. This indicates that a non-monotonic change in H_C with particle size should be attributed to the transition of the domain structure from single domain to multi-domain.

Keywords: A. Grain growth; B. Grain size; C. Magnetic properties; D. Ferrites

1. Introduction

The manipulation of magnetic properties on the nanometer scale has been previously conducted [1]. Given that the magnetic properties of nano-sized magnetic materials are very different from those of a bulk compound, research on the particle size dependence of the magnetic properties of nano-sized magnetic materials extends the horizons of the theory of magnetism.

With respect to their bulk counterparts, nanosized magnetic materials usually exhibit a smaller saturation magnetization (M_S) [2] and enhanced/reduced coercivity (H_C). This distinction is mainly attributed to the unique characteristics of nanomaterials, such as the non-ignorable breaking of bonds near and on a surface due to the large atomic percentage of cations on the surface. Additionally, when the particle size is reduced considerably, domain walls disappear and the entire particle forms a single domain, giving rise to superparamagnetism (zero H_C [3]) when the thermal energy is much greater than the magnetocrystalline anisotropy energy of the single-domain particle.

Among all the ferrimagnetic ferrites with a spinel structure ($MnFe_2O_4$; M = Fe, Co, Ni, and Mn), cobalt ferrite ($CoFe_2O_4$) is particularly significant owing to its larger magnetocrystalline anisotropy constant ($K_A = (1.8\text{–}3) \times 10^5$ J/m^3) [4]. Studies on the particle size dependence of the magnetic properties of $CoFe_2O_4$ nanoparticles have been widely reported. The non-monotonous change in H_C with particle size is observed with H_C reaching its maximum at a particle size of 30–40 nm [4–10]. However, the mechanism for this is still under debate. Some researchers attribute this maximum H_C to a watershed between the single- and multi-domain structure [5–10], whereas other researchers hypothesize that this non-monotonous change in H_C with the particle size may reflect

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the competition between thermal energy and surface anisotropy energy [4,11,12]. Thus, efforts that have been employed thus far to understand the particle size dependence of H_C are inadequate.

The different opinions of researchers in this regard may have originated from the difficulty in directly observing the domain structure of powdered samples. However, this issue can be resolved using the well-established fact that the magnetization processes of single-domain particles and multi-domain materials are very different. Single-domain particles are magnetized by rotating magnetic moments under an external magnetic field, whereas the movement of domain walls contributes considerably to the magnetization of multi-domain materials. This movement becomes irreversible when the strength of a field becomes greater than a critical value, thereby resulting in an enormous enhancement of magnetization (the so-called Barkhausen jump). Consequently, the characteristic analysis of magnetization curves (M–H) could be a valid method to indirectly determine the change in the domain structure. However, no study has been reported thus far which uses this methodology to verify the mechanism responsible for the observed change in H_C with the particle size.

In the present work, the particle size dependence of magnetism in $CoFe_2O_4$ nanoparticles has been studied in detail. When the size of the nanoparticles is near 40 nm, the H_C reaches its maximum, and a Barkhausen jump occurs, thus providing clear evidence for the transition between a single-domain and multi-domain structure.

2. Experimental method

$CoFe_2O_4$ precursor powders (denoted as sample *C*) were prepared using the combustion method reported in Ref. [8]. In order to prepare $CoFe_2O_4$ samples with different particle sizes, sample *C* was annealed at 300, 500, 600, and 1000 °C for 4 h in a muffle. According to their annealing temperatures, the samples are denoted as A-300, A-500, A-600, and A-1000, respectively.

X-ray diffraction (XRD) patterns were collected using a D8-Advanced X-ray diffractometer with CuKα radiation. The phase analysis data were obtained in the 2θ scanning range from 15° to 70° (1°/min) with the step size of 0.02° and from 32° to 35° (0.15°/min) at a step of 0.005°. Lattice constants were determined using the Bragg equation, while the average crystallite sizes were calculated using the Scherrer formula with a deduction to account for the instrument broadening. Fourier transform infrared transmission spectroscopy (FT-IR, NICOLET 5700) data was taken from 4000 to 400 cm^{-1} to determine the residual organic materials in sample *C*. The morphologies of the particles were observed using transmission electron microscopy (TEM, JEM2010). The magnetic hysteresis loops of the samples were collected at 300 K via a vibrating-sample magnetometer (VSM) on a physical property measurement system (PPMS-9, Quantum Design) under a maximum applied field of 20000 Oe.

3. Results and discussion

The FT-IR spectroscopy results of sample *C* is shown in Fig. 1. The peaks near 570 cm^{-1} is associated with the stretching vibration of the Fe–O bond in $CoFe_2O_4$ [5,8], while the peaks near 3430 and 1623 cm^{-1} are assigned to the stretching and bending vibrations of the H–O–H bond, respectively [5,8]. This shows the physical adsorption of H_2O on the nanoparticle surfaces. It was determined that none of the peaks from most of the organic groups, such as $(NO_3)^-$, $-$COOH, and H–O were detected [5]. In fact, only weak peaks of some residual groups, such as $-CH_2$ and –H–O–C, were found at 2860, 2925, and 1100 cm^{-1} [8]. This indicates that the amount of the residual organics in sample *C* is very small.

Fig. 2 shows the XRD patterns of sample *C* and samples after annealing, while the inset figures show the magnified ones between 32° and 35°. Most of the peaks can be indexed

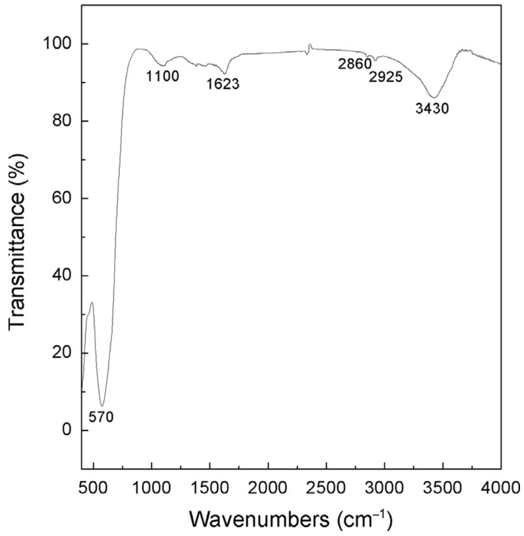

Fig. 1. FTIR spectra of the sample before annealing.

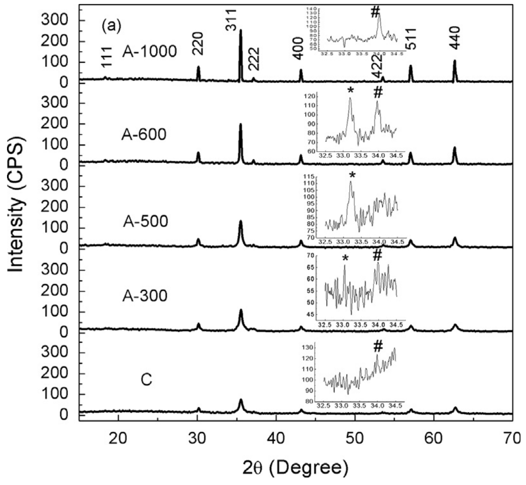

Fig. 2. XRD patterns of the samples before and after annealing (The inset figures show the magnified spectra between 32.5° and 34.5° by slow scan.).

Table 1
The lattice constants, crystallite sizes, and magnetic properties of $CoFe_2O_4$ samples before and after annealing.

Sample	Lattice constant (Å)	Average size (nm)	Ms (emu/g)	Hc (Oe)	K_{eff} ($10^5 J/m^3$)	χ_p (10^{-5}emu/g Oe)
C	8.383 ± 0.005	15 ± 1	53.2 ± 0.1	734 ± 12	7.1 ± 0.2	8.0 ± 0.2
A-300	8.380 ± 0.005	29 ± 1	59.27 ± 0.04	1341 ± 20	7.3 ± 0.1	6.11 ± 0.06
A-500	8.384 ± 0.005	39 ± 1	69.46 ± 0.07	1546 ± 3	7.6 ± 0.1	5.42 ± 0.07
A-600	8.387 ± 0.005	115 ± 11	74.98 ± 0.06	1268 ± 15	5.6 ± 0.2	2.71 ± 0.08
A-1000	8.389 ± 0.005	> 1 μm	89.8 ± 0.4	677 ± 4	5.0 ± 0.3	1.9 ± 0.1

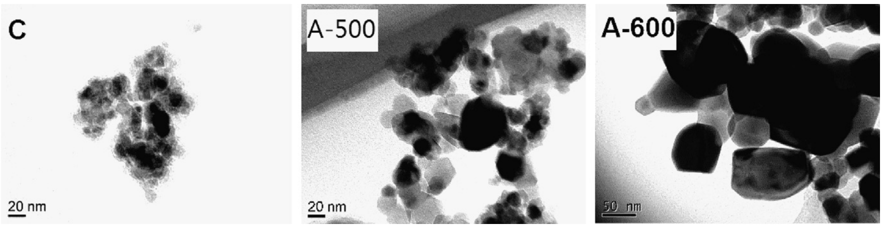

Fig. 3. The TEM images of the samples before and after annealing at 500 and 1000 °C.

from the JCPDS card of $CoFe_2O_4$ (No. 22-1086), and weak peaks of α–Fe_2O_3 (labeled by & and #) were also detected. This indicates the formation of a small amount of α–Fe_2O_3 [5]. The lattice constant and average crystallite size data are listed in Table 1. For sample C, the lattice constant is 8.383 ± 0.005 Å and average crystallite size is approximately 15 nm. For samples A-300 and A-500, the particle sizes remain in the nanosize range (30–40 nm). However, for samples A-600 and A-1000, a significant increase in the particle sizes was found.

The TEM images of samples C, A-500, and A-600 are shown in Fig. 3. It can be seen in sample C that the aggregated nanoparticles smaller than 20 nm have irregular shapes and rough surfaces. Meanwhile, in sample A-500, many particles have clear-cut edges with increased sizes of 30–40 nm. This indicates a grain growth with improved crystallization. For sample A-600, the TEM analysis revealed a clear increase in particle sizes, which is consistent with the XRD results.

The magnetic hysteresis loops measured at 300 K are shown in Fig. 4. The magnetic properties including M_S, effective magnetic anisotropy constant (K_{eff}), and high-field paramagnetic susceptibility (χ_p) were obtained by fitting the magnetization data at high fields (near 20000 Oe) using the law of approach to saturation [4,13,14]:

$$M = M_S - \frac{0.07619K_{eff}^2}{M_S H^2} + \chi_p H,$$

where M is magnetization and H is the strength of the applied magnetic field. A coefficient of 0.07619 was used due to the cubic anisotropy of $CoFe_2O_4$ [14]. The H_C were determined by a linear fit of the data near $M=0$ emu/g.

All magnetic parameters are also listed in Table 1. It can be seen that the M_S of sample C is 53 emu/g, which is approximately 30 emu/g smaller than the bulk $CoFe_2O_4$ [4]. The H_C of sample C is 734 Oe, which is close to the H_C of the $CoFe_2O_4$ nanoparticles prepared via similar methods [5,8]. The K_{eff} of sample C reaches 7.1×10^5 J/m^3, which is larger than the K_A of $CoFe_2O_4$ ($(1.8–3) \times 10^5$ J/m^3 [4,15]), while the χ_p of sample C is as large as 8.0×10^{-5} emu/g Oe.

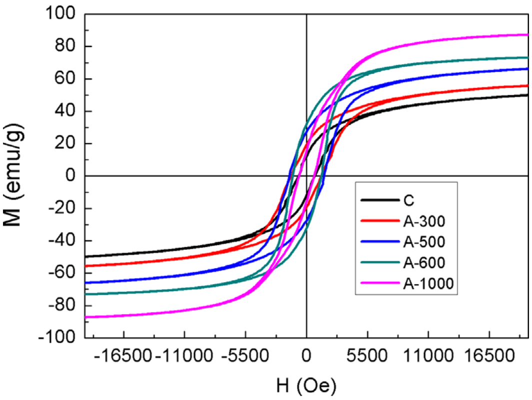

Fig. 4. The room-temperature hysteresis loops of the samples before and after annealing.

The low M_S of sample C could be attributed to the weak response of the magnetization from a "dead-magnetization layer" on a particle surface with disordered spins, as is often found in nanoparticle materials [4]. In this work, the small amount of α-Fe_2O_3 may also be contributed to the low M_S. However, as indicated by the XRD patterns, this impure phase was not eliminated by annealing. Therefore, it is reasonable to think that surface the effect may play a vital role in the low M_S of sample C.

In addition, it can be seen in Table 1 that the changes of K_{eff} and H_C with particle size are not monotonous, and both parameters exhibit a maximum value around 40 nm. When it comes to the effective magnetic anisotropy energy of nanosized materials, besides the intrinsic magneto-crystalline anisotropy energy, some other extrinsic free energies, such as the shape, strain, and surface anisotropy energies should be taken into account [4,6,14]. Therefore, the non-monotonous changes of K_{eff} with particle size can be assigned to the competition among these free energies. For example, magneto-crystalline and shape anisotropy energies may be enhanced after annealing due to the special shape and better crystallization of the bigger particles, but the surface anisotropy energy can be greatly reduced with increasing particle size. The mechanism for the non-monotonous change in H_C with particle size is still under debate. Some researchers attribute it to the competition between the thermal and surface anisotropy energies [4,11,12], while others believe that the maximum H_C means a watershed between the single- and multi-domain structures [5–10]. Although the direct observation of the domain structure of powdered specimens is difficult, it is possible to clarify the mechanism by observing the Barkhausen jump (an abrupt increase of magnetization) in the initial magnetization curve (M–H) of multi-domain materials. This phenomenon can be experimentally confirmed using the appearance of a peak in the differential susceptibility (dM/dH)–magnetic field (H) curve. In addition, the field for this peak (H_0) is proportional to the inverse of M_S [16]. Therefore, the dM/dH–H curve may also provide information regarding the domain structure transformation in magnetic materials.

Fig. 5(a) and (b) shows the M–H and dM/dH–H curves with fields ranging from 0 to 5000 Oe. Clearly, for the samples annealed at temperatures greater than 300 °C, the M–H curves show inflection under certain fields, which is accompanied by the appearance of the peaks in the dM/dH–H curves. As the annealing temperature increases, these peaks increase and shift to lower fields. As shown in the inset figure in Fig. 5(b), there is a consistent linear relationship between H_0 and $1/M_S$. However, for samples C and A-300, which have a lower M_S, we cannot detect the inflection or peaks at fields larger than sample A-500. Therefore, it can be concluded that a transformation of the domain structure from a single domain to multi-domain occurs around 40 nm. Additionally, when the sizes are larger than 100 nm, the irreversible displacement of domain walls has a major contribution to the magnetization process.

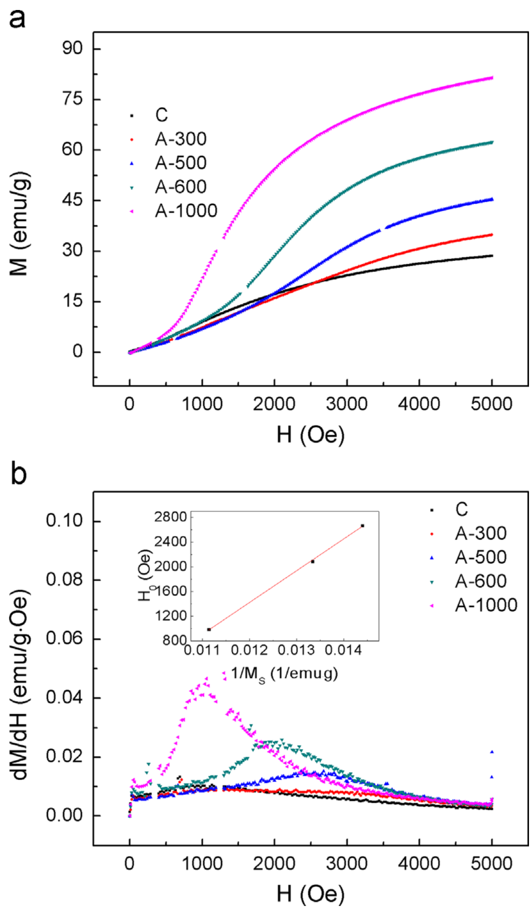

Fig. 5. (a) Initial magnetization curves and (b) dM/dH–H curves of samples before and after annealing (The inset figure in (b) shows the relationship between the field for the peak and $1/M_S$).

4. Conclusions

In conclusion, annealing the powdered $CoFe_2O_4$ nanoparticles synthesized using the combustion method from 300 to 1000 °C led to an increase in the particle sizes from 15 nm to >1 μm. The M_S increased with particle size; however, H_C reached its maximum close to 40 nm, which was accompanied by the appearance of a Barkhausen jump in the initial M–H curve. This provided clear evidence that the maximum H_C was attributable to the transition from a single-domain to a multi-domain structure.

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