Magnetic properties of core/shell-structured CoFe$_2$/CoFe$_2$O$_4$ composite nano-powders synthesized via oxidation reaction

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Abstract

The CoFe$_2$/CoFe$_2$O$_4$ composite is a new type of exchange-spring magnet that has attracted much attention in recent years. To resolve the unstable chemical properties for CoFe$_2$/CoFe$_2$O$_4$ composite nanoparticles with CoFe$_2$ shells prepared by reducing CoFe$_2$O$_4$, we synthesized core/shell-structured CoFe$_2$/CoFe$_2$O$_4$ composite nanoparticles with CoFe$_2$O$_4$ shells by oxidizing CoFe$_2$ nanoparticles. The composition and micro-structure of the composite were characterized using an X-ray diffractometer, a transmission electron microscope and a high-resolution transmission electron microscope. Magnetic measurements, including magnetic hysteresis loops, Henkel plots, and temperature-dependent magnetization curves, were performed using a vibrating sample magnetometer. The results showed that the nanoparticles were composed of CoFe$_2$ cores and CoFe$_2$O$_4$ shells, and a regular non-monotonous variation of properties was found. When the mass percentage of CoFe$_2$O$_4$ was 30%, the average crystallite size of CoFe$_2$ reached its maximum value, a minimum coercivity was observed, and the exchange coupling between CoFe$_2$ and CoFe$_2$O$_4$ was strengthened. This non-monotonous change in properties is attributed to the lattice vacancies and spin-glass-like state occurring when the mass percentage of CoFe$_2$O$_4$ is very small and dominant hard magnetic behavior exists in the larger CoFe$_2$O$_4$ phase.

Keywords: Composite materials; Exchange-spring effect; Oxidation reaction; Magnetization

1. Introduction

The exchange-spring (ES) effect in hard-magnetic (HM)/soft-magnetic (SM) composite materials is a reversible demagnetization behavior due to exchange coupling at the HM/SM interface [1–2]. In contrast to the conventional rigid-magnetism (RM) phase, an ES magnet exhibits a much smaller switching field without sacrificing thermal stability, which is vital to information storage [3]. Additionally, the maximum magnetic energy product of an ES magnet is larger than that of a conventional permanent magnet, which is favorable to increase the energy stored in a magnet [1].

Thus far, many variations of ES magnets have been synthesized, such as Nd–Fe–B/Fe–B, [2] CoFe$_2$O$_4$/Fe$_3$O$_4$, [4,5] Ba-ferrite/Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$, [6] Ba-ferrite/Fe$_3$O$_4$, [7] and FePt/Fe [8–10]. Since 2011, CoFe$_2$O$_4$/CoFe$_2$ has attracted attention as an ES magnet because it exhibits a large difference in magnetism between the SM CoFe$_2$ and HM CoFe$_2$O$_4$ phases and its synthesis is easy [11–18]. CoFe$_2$O$_4$ exhibits large magnetocrystalline anisotropy and a moderate saturation magnetization ($M_s$), and CoFe$_2$ has a very small coercivity and larger $M_s$. Therefore, the CoFe$_2$O$_4$/CoFe$_2$ ES magnet may be an ideal candidate for future magnetic storage media. In 2011, Soares et al. successfully fabricated CoFe$_2$O$_4$/CoFe$_2$ nanoparticles consisting of CoFe$_2$O$_4$ cores and CoFe$_2$ shells by reducing CoFe$_2$O$_4$ nanoparticles in H$_2$, and they reported that...

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inter-phase exchange coupling is significantly strengthened when the thickness of the CoFe2 shell exceeds a critical value [11].

In addition to the ES effect in composite nanoparticles with CoFe2O4 cores and CoFe2 shells, the ES behavior in composite nanoparticles with an inverse structure, CoFe2 cores and CoFe2O4 shells, deserves investigation. First, the outer CoFe2O4 shell is chemically stable. On the other hand, the interplanar spacing of CoFe2 is very similar to that of CoFe2O4 oxidized from CoFe2 [19], which may be beneficial for coupling on the atomic scale at the CoFe2O4/CoFe2 interface. In 2010, Jaffari et al. reported an investigation on the synthesis of core/shell-structured CoFe2O4/CoFe2 nanoparticles by oxidizing CoFe2 and the surface and spin-glass-like state for the amorphous CoFe2O4 shell [22]. However, the ES effect due to the exchange coupling at the interface between CoFe2 and CoFe2O4 has not been reported yet.

In the present work, CoFe2/CoFe2O4 composite nanoparticles consisting of CoFe2 cores and CoFe2O4 shells were fabricated by oxidizing CoFe2 nanoparticles prepared in advance. Variations in magnetic parameters and inter-particle/phase magnetic interaction in response to the variations in the mass ratio are studied in detail. We found and attempted to explain an interesting regular non-monotonous change in physical properties with the mass ratio.

2. Experimental method

CoFe2O4 precursor powders were first prepared using the combustion method with annealing at 400 °C to remove residual organics [17]. Subsequently, the CoFe2 powders (labeled CF) were synthesized by completely reducing the CoFe2O4 precursor at 400 °C for 300 min in a N2/H2 mixed atmosphere (10 vol% H2). We determined whether the reducing reaction was complete by measuring the mass change of the powders due to the reducing reaction. Finally, the CoFe2 powders were oxidized at 380 °C in a pure O2 atmosphere. The mass percentages for CoFe2O4 were tuned by adjusting the reaction time (3 min, 10 min, 15 min, 120 min and 600 min) and were determined by measuring the change in mass.

X-ray diffraction (XRD) patterns of all the powders were collected using a D8-Advanced X-ray diffractometer with CuKα radiation. The 2θ scanning range was between 15° and 70° (4°/min), and the step size was 0.02°. Scanning at approximately 35° and 45° at a slower rate (0.5°/min) and with a smaller step size (0.005°) was also conducted by depleting the background signal and with the data from the X-ray with CuKβ and CuKα2 radiation, and the data of the peak position and full-width at half maximum (FWHM) were refined using Topas software. Based on the peak positions and FWHM, the average crystalline sizes of CoFe2O4 and CoFe2 were calculated using the well-known Scherrer formula. The morphology and micro-structure of particles in the samples were characterized using a transmission electron microscope (TEM, JEM2010) and a high-resolution TEM (HRTEM, JEM2010 FEF). The magnetic properties were measured using a vibrating sample magnetometer on a physical-property measurement system (PPMS-9; Quantum Design). Magnetic hysteresis loops were measured at 300 K and 10 K from −50,000 Oe to 50,000 Oe, and the Henkel plots (δm) were obtained at 300 K. The sample used for measuring every δm measurement had not been magnetized before the measurement. The measurement procedure for δm has been described in detail in Ref [16]. Additionally, after a zero-field-cooling (ZFC) procedure from 300 K to 10 K, the temperature-dependent magnetization (M−T) was also investigated under 50,000 Oe from 10 K to 300 K.

3. Results and discussion

The measurement of mass change indicated that the mass percentages for CoFe2O4 in the samples prepared by oxidizing CoFe2 at 380 °C for 3 min, 10 min, 15 min, 120 min and 600 min are 18%, 30%, 56%, 78%, and 93%, respectively; the corresponding samples are labeled 18CFO, 30CFO, 56CFO, 78CFO and 93CFO.

The XRD patterns of all the samples are shown in Fig. 1(a), and the patterns for scanning near 35° and 45° are shown in Fig. 1(b) and (c), respectively. In the XRD pattern of sample CF, all the peaks can be indexed from the Joint Committee on Powder Diffraction Standards (JCPDS) card of CoFe2 (No. 03-065-4131), and only traces of the CoFe2O4 phase were detected. For sample 18CFO, although the peak intensity of the (110) main peak of CoFe2 was significantly reduced, the (311) main peak of CoFe2O4 was not noticeably strengthened, which is attributed to the poor crystallization of CoFe2O4. When the mass percentage for CoFe2O4 was 30% or higher, the (311) main peak of CoFe2O4 was clearly observed, and the (110) main peak of CoFe2 was further reduced. When the mass percentages reached 78% and 93%, the peaks of CoFe2 became quite weak.

Note that in addition to CoFe2O4 and CoFe2, no other phase was detected in the XRD patterns. Such good purity seems to be an advantage of the oxidation reaction because some impure phases, such as Co, FeO, and other phases that are not indexed, are always detected using XRD for CoFe2O4/CoFe2 composite materials prepared by reducing CoFe2O4 [13,16,17].

The estimated average crystallite sizes of CoFe2O4 and CoFe2 in the samples are listed in Table 1. For samples 78CFO and 93CFO, the average CoFe2 crystallite size was not calculated because its peak is too weak to be differentiated from noise. As indicated in Table 1, the average crystallite sizes of CoFe2O4 in all the samples are near 15 nm, and a small size increase was observed when the CoFe2O4 phase becomes dominant, indicating that the oxidation reaction is not quite helpful to crystallize CoFe2O4. On the other hand, the average crystallite sizes of CoFe2 are clearly related to the mass percentage of CoFe2O4, and a regular non-monotonous change of the average crystallite size of CoFe2 with the mass percentage of CoFe2O4 was observed. With the increase in the mass percentage of CoFe2O4, the average crystallite size of CoFe2 first increased, reaching its maximum value when the mass percentage of CoFe2O4 was 30%; with further increase in the mass percentage of CoFe2O4, the average crystallite size of CoFe2 decreased. In Ref. [17], which concerns the synthesis of CoFe2O4/CoFe2 composite materials by reducing CoFe2O4, a