Synthesis and magnetic properties of chromium doped cobalt ferrite nanotubes

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Abstract
Chromium (Cr) doped cobalt ferrite (Co1-xCrxFexO4; x = 0.0, 0.02, 0.04, 0.06, 0.08, 0.1, denoted as to CCFO) hollow nanotubes were synthesized by electrospinning method followed by calcining treatment at 700 °C in air. The samples exhibited a single phase cubic spinel phase. The lattice constant of the samples was found to initially decreased and thereafter increases with increased of Cr content. The morphology analysis indicated that the samples displayed a disordered arrangements of hollow structures and the relevant surfaces were rough and porous. Transmission electron microscopy (TEM) paragraph confirmed that the doped CCFO nanotubes had a polycrystalline nature and exhibited the changes in the corresponding crystal structure. X-ray photoelectron spectroscopy (XPS) confirmed that Cr doping affect the crystal structure and atomic-binding energy. The analysis of magnetic hysteresis loop indicated an obvious reduction in the saturation magnetization (Ms) of cobalt ferrite with increasing in Cr substitution. The remanent magnetization (Mr) and coercivity were increased at first and then decreased with increasing of Cr content, which was elucidated by the surface effect and magnetic moment direction. The switching field distribution analysis indicated the magnetically crystal soft phase and there were multiple-step processes to reach magnetic reversal.

1. Introduction

With the advancement of speed-driven data storage technology, cobalt ferrite magnetic nanomaterials have been paid extensive attention due to their wide applications in wired communications, high density magnetic recording media, microwave devices, wireless communications, aerospace technology and so on [1–3]. There are eight formula units per unit cell for AB2O4 spinel ferrites, whereas the larger oxygen anions comprise a crowded face-centered-cubic structure and the smaller metal cations occupy the interstitial positions. Moreover, compared with metals, cobalt ferrite is the most appropriate hard ferromagnetic material, displaying characteristics such as high Curie temperature Tc (~520 °C), larger magnetocrystalline anisotropy, a high coercivity value, moderate saturation magnetization (~70 emu g⁻¹), high magneto-optic Kerr effect, and Faraday rotation [4–6]. Cobalt ferrite (CoFe2O4) has been applied in read-write heads of hard disks and other memory devices because of its outstanding applications in electronic storage areas [7, 8]. CoFe2O4 nanofibers have neither absolutely normal spinel structure nor completely inverse spinel structure, but they have a mixed spinel structure [9, 10]. Other studies indicated that CoFe2O4 revealed an inverse spinel structure with the cobalt ions showing a preference for octahedral connected B sub-lattice while Fe³⁺ ions occupied A and B sub-lattices, respectively [11, 12]. Net magnetic moment could be generated from the unequal distribution of spins between A site and B site, which leads to a ferromagnetic nature. Furthermore, the majority of empty interstitial sites between A site and B site are occupied by the suitable divalent or trivalent cations and the ferromagnetic behavior of ferrites is required to adjust according to practical demands. The electron configuration of the trivalent transition element, such as Cr, is 3d⁵4s¹, which has attracted more researchers to investigate [13, 14].

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Lee et al [15] reported Cr doped Ni spinel ferrite that Cr$^{3+}$ ions have a preference for the B site using the solid reaction method and presented an electron configuration of t$_{2g}^{2}$e$_{g}^{0}$ which indicated a larger orbital angular momentum in theory. Man Han et al [16] researched the magnetic properties of CoCrxFe$_{2-x}$O$_4$ spinel ferrite nanoparticles and discovered that the saturation magnetization, coercivity and remnant magnetization were decreased with increasing Cr content. Shang al [17] investigated the magnetic properties of the Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ nanoparticles by a hydrothermal method. The research suggested that the samples showed a single phase with a space group of Fd$ar{3}$m and the saturation magnetization was decreased with the increase of Cr substitution. Alina et al [18] studied the CoCrxFe$_{1.8}$O$_4$ powders by the co-precipitation method. The result showed that the nanoparticles were agglomerated and had polygonal faced surfaces, and the crystallite size was ranged from 44 to 79 nm. The saturation magnetization had a slight increase and the coercivity was increased after doping with Cr ions. Lawrence Kumar [19] researched the magnetic relaxation of CoFe$_{2-x}$Cr$_x$O$_4$ nanoparticles using the standard citrate precursor method and the result demonstrated that the saturation magnetization and magnetocrystalline anisotropy were increased with increasing Cr content. Kombaiah et al [20] investigated the morphology and magnetic properties of CoFe$_2$O$_4$ nanoparticles by a conventional and microwave heating method. The results demonstrated that the decrease in the crystallite size led to a decrease in saturation magnetization. The result might be associated with the structural distortion. Bagade et al [21] investigated the structural and magnetic properties of CoFe$_2$O$_4$ thin films using a spray pyrolysis technique. This study showed that the formation of the spherical grain structure of CoFe$_2$O$_4$ thin films is useful for gas sensing application. To the best of our knowledge, although the previous studies have attached much attention to the chromium doped cobalt ferrite nanoparticles, the magnetic properties of Cr-doped CoFe$_2$O$_4$ hollow nanotubes by an electrospinning method have not been reported yet in the literature.

In this article, we have synthesized a series of cobalt ferrite doped with Cr element with the generic formula Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ with ‘x’ in the range of 0.0–0.1 using electrospinning method. X-ray diffraction manifested the cobalt ferrite nanotubes of the spinel phase without any additional peaks. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to characterize the microstructure and morphology. The magnetic properties were characterized by physical property measurement system (PPMS). The particular efforts were put on the influence of different contents of Cr and discussed the influence of magnetic anisotropy on the relevant magnetic properties. The dopants of metal cation with different valence state could tailor magnetic properties and Curie temperature for the specific applications.

2. Experiments

Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ (x = 0.0–0.1) hollow nanotubes were synthesized using double spray nozzles with the same coaxial by an electrospinning method. Firstly, the reagents Co(NO$_3$)$_2$.6H$_2$O (AR, 99%), Cr(NO$_3$)$_2$.6H$_2$O (AR, 99%), and Fe(NO$_3$)$_3$.9H$_2$O (AR, 99%) were mixed in a stoichiometric ratio by keeping cations to molar ration of 1–x : x : 2 and added to 3.6 g polyvinylpyrrolidone (PVP, Mw = 1300 000). The mixed solution as one precursor treated as shell was stirred 12 h in a magnetic stirrer while 3 ml ethanol and 2 ml dimethylformamide (DMF) were added. Another precursor as core was prepared with 5 ml ethanol and 3.6 g PVP regarded. Secondly, the pseudo-solution was supplied through the double spray nozzles with the same coaxial attached to a stainless steel needle tip, which was connected to a high-voltage power supply. High direct current voltage of 18 kV was connected between a piece of needle and flat aluminum foil placed 18 cm to collect the nanotubes. The as-spun speed rate of precursor was 0.3 ml h$^{-1}$. Finally, the obtained nanotubes were calcined at 700 °C with a heating rate of 1 °C min$^{-1}$ in air and then transferred into a mortar agate for manually grinding process. The samples were obtained after cooling down at room temperature.

The crystal structures of the nanotubes was investigated by x-ray diffraction (XRD) on a Rigaku d/θ/2θ rotating diffractometer. The XRD analysis data were collected in 2θ degree range of 20°–80°. The microstructure of the nanotubes was characterized using scanning electron microscope (JEM-6701F) and transmission electron microscopy (JEM-1200EX). X-ray photoelectron spectroscopy (XPS) spectra for the samples were measured by Thermo Scientific ESCALAB XI+. The magnetic parameters measurement of the samples was performed using Model-9 Physical Property Measurement System (PPMS).

3. Results and discussion

3.1. Structural properties

Figure 1 presents XRD patterns for Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ (x = 0.0–0.1) ferrite systems. X-ray diffraction patterns indicated that the pure crystalline phase was obtained after the precursors were calcined at 700 °C. All the diffraction peaks are indexed to a spinel structure with a space group of Fd$ar{3}$m (ICPDS card No. 22-1086). The average diameters of these nanotubes is compiled in table 1. The XRD data are fitted by using Rietived powder.
diffraction profile fitting technique [22] using the X’ Pert HighScore Plus software. The lattice constant $a$ was obtained using only main peak of (311) plane based on the following formula [23]:

$$a = d\sqrt{h^2 + k^2 + l^2}$$  \hspace{1cm} (1)

where $(h k l)$ are the Miller indices, and $d$ is the inter-planar spacing. Figure 2 showed the variation of lattice constant with the Cr content. It can be seen from figure 2 that the variation of lattice constant was non-linear. The non-linear variation of lattice of constant indicated that the CCFO ferrite system was not completely normal or inverse [24, 25]. For the spinel structure, the ideal values of $d_{AO}$, $d_{BO}$, and $d_{AB}$ are $\sqrt{3} a/8$, $a/4$, $\sqrt{11} a/8$, respectively, which $d_{AO}$ and $d_{BO}$ are the distance between O anion and the cations at the A and B site, $d_{AB}$ is the

| $x$  | $D$/nm  | $a$/Å  | $d_{AO}$/Å | $d_{BO}$/Å | $d_{AB}$/Å |
|------|---------|--------|------------|------------|------------|
| 0.02 | 126.25  | 8.373  | 1.895      | 2.035      | 3.481      |
| 0.04 | 133.25  | 8.352  | 1.891      | 2.030      | 3.473      |
| 0.06 | 135.62  | 8.342  | 1.889      | 2.027      | 3.468      |
| 0.08 | 117.65  | 8.341  | 1.888      | 2.027      | 3.468      |
| 0.10 | 112.59  | 8.356  | 1.892      | 2.031      | 3.474      |

Figure 1. XRD patterns of the samples with different Cr contents calcined at 700 °C.

Figure 2. Variation of lattice constant and x-ray density with Cr content.
distance between the cations at the A and B sites (see table 1). However, the observed values of all samples of $d_{AO}$ and $d_{BO}$ in table 1 are 1.076 and 0.972 times the ideal values, respectively, while the value of $d_{OB}$ is equal to its ideal value. Meanwhile, the results from X’ Pert HighScore Plus software indicated that the volume-averaged diameter of the samples is larger than 110 nm, which is consistent with the data from analysis of the SEM images. The $d_x$ is the x-ray density with the following relation [26]:

$$d_x = \frac{8M}{Na^2}$$  \hspace{1cm} (2)

where $M$ is the molecular weight, $N$ is Avogadro’s number ($6.0225 \times 10^{23}$ particles mole$^{-1}$), and $a$ is a lattice constant. Figure 2 revealed that the variation of x-ray density had the reverse variation tendency compared to the variation of lattice constant, considering that the $d_x$ is inverse to the lattice constant $a^2$. Table 1 revealed that the average diameter of CCF0O nanotubes increased to the maximum and then decreased with the Cr content increased. The value of diameter ranges from 112.59 nm to 126.25 nm. The type of catalysts had an effect on the diameter of the nanotube and the catalytic activity of those nanotubes depend on cation distribution in the octahedral and tetrahedral sites, structural isotropy, and catalytic activity due to cations [27]. The process of catalytic production and temperature also affect the morphology and diameter of spinel ferrite nanobars [28]. The crystal structure of the nanotube arrays were controlled by heating treatment progresses [29] and indicated that nanotubes arrays with outer diameter of 200 nm exhibit magnetic anisotropy. Some evidence indicated that the phenomenon [30] of variation of diameter is attributed to the microstrains existing in the crystalline lattice. Thus, the variation of the average diameter of spinel ferrites samples would be attributed to the heating temperature, cation distribution and so on. In a complex system of spinel ferrites, there are many cations are involved, the nucleation and growth of the samples are expected to be influenced by the probability of a cation occupying available chemically in equivalent sites [31]. In this study, Cr$^{2+}$ and Cr$^{3+}$ ions have strong preferential occupy towards octahedral site. Cr$^{2+}$ (0.80 Å) ions have larger ionic radii compared to Co$^{2+}$ (0.74 Å) and Fe$^{2+}$ (0.78 Å) ions, part of Cr$^{2+}$ ions occupy at tetrahedral site when the Cr content is low. The tetrahedral site has slightly less space than octahedral site. This may be lead to the particle size of samples increases with increase in Cr content. On the contrary, Cr$^{3+}$ (0.62 Å) ions gradually occupy the octahedral site with Cr content increases, which may be lead to the decrease of particle size.

### 3.2. The variation of the lattice constant analysis

In the tradition theory, CoFe$_2$O$_4$ has an inverse spinel structure where 8 Fe$^{3+}$ cations occupy A sites, and other 8 Fe$^{3+}$ and 8 Co$^{3+}$ cations occupy B sites. The magnetic moment at the A sites are antiparallel to those at the B sites, because of existing the super-exchange interaction between cations at the A sites and cations at the B sites, which is caused by oxygen anions [32–34]. However, the distribution of Cr cations in the spinel ferrites has an obvious discrepancies [35–37]. The cations distribution of CoFe$_2$O$_4$ and CoCr$_{0.2}$Fe$_{1.8}$O$_4$ samples discussion indicated that all Cr cations entered into the B sites and part of the Co cations migrated to the A sites from the B sites, which lead to cation distribution in the form of (Co$_{0.65}$Fe$_{0.35}$)Cr$_{0.2}$O$_4$ and (Co$_{0.17}$Fe$_{0.83}$)Co$_{0.85}$Cr$_{0.15}$O$_4$ [29]. Chae et al [38] considered that the total Cr cations entered into the B sites, and part of Co cations migrated to the B sites from the A sites, resulting in cation distribution in the form (Co$_{0.65}$Fe$_{0.35}$)Cr$_{0.2}$O$_4$ and (Co$_{0.33}$Fe$_{0.67}$)Co$_{0.67}$Cr$_{0.33}$O$_4$. In our opinion, there are some characteristics of the Cr cations, which different from those of Fe, Co, and Ni: the numbers of 3d electrons in Cr$^{3+}$ and Cr$^{2+}$ are 3 and 4, respectively, which lead to the magnetic moments of Cr cations being antiparallel to those of Fe cations [39]. In order to better understand the cation distribution of Co$_{1-x}$Cr$_{x}$Fe$_2$O$_4$, based on the quantum mechanical model [40], the results indicate that the number of Cr$^{2+}$ and Cr$^{3+}$ cations at the A sites and B sites increase linearly with increasing of Cr content. Meanwhile, the concentration of Cr$^{2+}$ cations at the B sites is larger than those of Cr$^{3+}$ at the B sites, Cr$^{2+}$ and Cr$^{3+}$ at the A sites, which is consistent with the results by Kriebel [41] and Magalhaes [42] reported.

Generally speaking, the O 2p electron of oxygen anion serve as intermediaries for the itinerant 3d electrons. The magnetic moments of Fe and Co cations are parallel, which lead to a magnetic repulsion energy. The magnetic moment directions of Cr$^{2+}$ and Cr$^{3+}$ are antiparallel to the directions of Fe and
Co cations, which resulting in the change of magnetic repulsion energy, and also causing the lattice constant to decrease with increasing of Cr cations [17]. Secondly, the distance (d_{AO}) from O anion to the cations at the A sites is larger the ideal values, and the distance (d_{BO}) from O anion to the cations at the B sites is smaller than the ideal value. The number of divalent cations at the A site increases and the number of trivalent cations at the A sites decreases. It is well known [39] that the effective radii of the Cr^{2+}, Fe^{2+}, and Co^{2+} cations are 0.80, 0.78, and 0.74 Å, which is larger than those of the corresponding trivalent cations (0.62, 0.64, and 0.61 Å). Thus, the increase of the lattice constant of the samples is determined by the increase of the number of divalent cations and the decrease of the number of trivalent cations at the A sites. As shown in figure 1, as the Cr-doped level x increases, the lattice constant decreases when x < 0.08, whereas it increases when x > 0.08. This is due to the smaller radii of substituted ions (Fe^{3+}: 0.64 Å, Cr^{3+}: 0.62 Å), which lead to the decrease of lattice constant. With increasing of Cr content, part of Cr^{2+} (0.80 Å) substituted Fe^{2+} (0.78 Å) and Co^{2+} (0.74 Å), which result in the increase of lattice constant.

3.3. Morphology analysis

Figure 3 exhibits SEM image with a low magnification of typical sample Co_{0.94}Cr_{0.06}Fe_{2}O_{4} (x = 0.06). This image was used to determine the chemical composition of samples by energy dispersive x-ray spectroscopy (EDS) and depicted the microstructure of Co_{0.94}Cr_{0.06}Fe_{2}O_{4}. As displayed by figure 3, the CCFO (x = 0.06) was consisted of iron, cobalt, chromium and oxygen elements, which was consistent with XRD analysis.

The microstructure of Co_{0.96}Cr_{0.04}Fe_{2}O_{4}, Co_{0.94}Cr_{0.06}Fe_{2}O_{4} and Co_{0.92}Cr_{0.08}Fe_{2}O_{4} nanotubes characterized by SEM presented in figures 4(a)–(c), respectively. With increasing of the Cr content, the unusual surface microstructure was clearly observed. It can be seen from SEM images diagrams that the samples exhibit a disorder arrangement of the hollow structures and the corresponding surfaces are rough and porous (figure 4(b)). These characteristics are attributed to the electrospinning process, take into account the extremely high calcination...
temperature that would result in releasing large amounts gas during the calcining process. With the increasing of Cr content, the surface of chromium doped cobalt ferrite nanotubes becomes more compact and smooth.

Figures 5(a) and (b) present the selected area electron diffraction (SAED) patterns along with TEM images of the Co0.94Cr0.06Fe2O4 nanotubes annealed at 700 °C. The average diameter of Co0.94Cr0.06Fe2O4 nanotubes was estimated to be 121 nm. The microstructure in figure 5 exhibited that some particles with irregular shapes were incorporated into the surface of samples. Figure 5 demonstrated that the nanotubes had a polycrystalline nature. Compared with the paragraph of figures 5(a) and (b), the crystal diffraction ring of gray areas is more crowded than the black areas. This is indicated that the lattice constant increased with increasing the Cr content leading to the change of the crystal structure.

3.4. XPS analysis
X-ray photoelectron spectroscopy (XPS) spectrum of Co0.92Cr0.08Fe2O4 nanotubes are showed in figure 6. It can be seen from images that the samples confirmed the existence of Co, Fe, and Cr. The binding energy of Co 2p$_{1/2}$ and 2p$_{3/2}$ has a more than 15.0 eV energy gap, exhibiting the coexistence of Co$^{3+}$ and Co$^{2+}$ in Co$_{0.92}$Cr$_{0.08}$Fe$_2$O$_4$ nanotubes [45]. As shown in figure 6(b), the peaks at 712.5 eV and 725.8 eV, which ascribed to Fe$^{3+}$ ions [46]. Two pronounced peaks at 576.8 eV and 584.6 eV were observed, corresponding to Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$, respectively, which ascribed to Cr$^{3+}$ ions [47]. The results indicate that Cr$^{2+}$ ions are unstable and more easily oxidized to Cr$^{3+}$ ions with increases of Cr content. Based on the above discussions, Cr doping affect the crystal structure and atomic-binding energy of CoFe$_2$O$_4$ nanotubes.

3.5. Magnetic properties analysis
Magnetic hysteresis loops at room temperature of the nanotubes were manifested in figure 7. The samples showed ferromagnetic behavior. Inset image of figure 7(f) revealed an enlarged curve of the M-H loops in the field range from $-6$ kOe to $+6$ kOe. The values of magnetic properties are showed in table 2. The saturation magnetization ($M_S$) decreased with increasing of Cr content. The super-exchange interaction plays an important role in the variations in the magnetization of the nanoferrites. In spinel ferrites, the saturation magnetization was attributed to the super-exchange interactions between the cations of the A sites and B sites. The strength of super-exchange interaction decreases as the Cr content increase [48]. The exchange interactions between A and B sites reduced due to the A-A interaction enhanced and A-B interaction weakened, which resulted in the decrease of $M_S$ [49]. On the other hand, according to the Neel's model [50], the A-B exchange interaction is dominated by the intra-sublattice A-A and A-B interactions. The net magnetization of ferrimagnetic material depends on cation distribution among octahedral and tetrahedral sublattice. The net magnetization at temperature can be written as [51]:

$$ M(T) = M_B(T) - M_A(T) $$

Where, $M_A(T)$ and $M_B(T)$ are the magnetization of B and A sublattices, respectively. According to the discussion of section 3.2, the net magnetic moment per unit for Cr$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Fe$^{2+}$, Co$^{3+}$ and Co$^2$ are $-3$ $\mu$B, $-4$ $\mu$B, 5 $\mu$B, 4 $\mu$B, 4 $\mu$B and 3 $\mu$B, respectively. It was found that Co$^{3+}$ and Cr$^{3+}$ ions have strong site preference for B sites while Fe$^{3+}$ have no particular preference for either coordination. The increase of Cr content led to minimize the number of Fe$^{3+}$ ions at these sites and consequently the net magnetic moment decreased, which resulted in the magnetization saturation decreases. Moreover, the structure was distorted at the surface and the atoms were under the effect of strain with Cr content, which led to vacancies, variety of
inter-atomic spacing and low coordination numbers. The results may induce a broken exchange bonds for the surface atoms which led to spin disorder \[52\]. The disordered spin may exhibit low magnetization. Meanwhile, magnetic anisotropy of cobalt ferrite was predominantly attributed to the single anisotropy of the B sites, and the shift of these ions from A site to B sites may bring up a decrease of magnetic anisotropy. Therefore, the substitution of Cr ions led to the decrease of the saturation magnetization and decreased the A-B interaction and altered the B-B interaction from ferromagnetic state to anti-ferromagnetic state. It has been well confirmed that the magnetic properties of spinel were stemmed from ferrites attributed to 3d electrons of the mental cations. As it is discussed in section 3.2, the numbers of 3d electrons in Cr\(^{3+}\) and Cr\(^{2+}\) were 3 and 4 respectively, which would make the magnetic moments direction of Cr\(^{3+}\) and Cr\(^{2+}\) cations become antiparallel to Fe and Co cations \[38\]. The distribution of Cr cation and increase of Cr content could decrease the value of magnetic moment, which leads to reduction in saturation magnetization.

As displayed in figure 8, the values of coercivity (\(H_C\)) increases first and then decreases with Cr content at 700 °C respectively. The variation of coercivity could be attributed to the presence of magnetic single domain in the samples annealed at 700 °C. In the single domain region the variation of coercivity with the crystallite size is expressed as \[23\]:

\[
H_C = g - \frac{h}{D^2}
\]  

(4)
where $g$ and $h$ are constant. It can be seen from equation (4), the variation of coercivity is consist with the change of crystallite size, which is consist with the description in figure 8. With increasing of Cr content, part of Co ions from octahedral migrate to tetrahedral sites. In cobalt ferrite the magnetic anisotropy predominantly arises from

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**Table 2. Magnetic properties of nanotubes.**

| $x$  | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (Oe) | $M_r/M_s$ |
|------|---------------|---------------|------------|-----------|
| 0.00 | 79.57         | 28.96         | 1001.12    | 0.364     |
| 0.02 | 71.26         | 29.76         | 1041.66    | 0.418     |
| 0.04 | 69.88         | 32.22         | 1284.72    | 0.461     |
| 0.06 | 68.81         | 34.12         | 1631.94    | 0.496     |
| 0.08 | 67.73         | 35.81         | 1875.42    | 0.529     |
| 0.10 | 67.11         | 33.17         | 1631.94    | 0.494     |

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**Figure 7.** Magnetic hysteresis loops measured at room temperature in air of $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nanotubes calcined at 700 °C.
the single-ion anisotropy of Co$^{2+}$ on the B sites, and the displacement of Cr ions should lead to a decrease of magnetic anisotropy and consequently to the decrease of the coercive field. In this study, the values of $H_C$ obtained for Cr substituted cobalt ferrite are higher than that of CoFe$_2$O$_4$.

Furthermore, the explanation for the decrease of $M_r$ and $H_C$ after Cr content up to $x = 0.08$ could be associated with the surface of the synthesized Cr-Co nanotubes. With the decreasing of the diameter size, the surface-to-volume ratio of the sample on the surface increased and the enhancement of the surface effect may induce a spin disorder in the superficial layer, which could similarly strengthen the surface anisotropy [53]. As the crystallite size decreases, the ratio of surface to volume atom increases as a result the surface effect becomes prominent. Structure is distorted at the surface and surface atoms are under the effect of strain which leads to vacancies, variety of interatomic spacing and low coordination numbers. These factors may cause a broken exchange bonds for the surface atoms which leads to spin disorder [31]. The disorder spin at the surface may exhibit low magnetization. With the increasing of Cr content, the decrease in magnetization could cause the material to be transformed into a soft magnetic material, which leads to the decrease of $H_C$.

Figure 9 presented the switching field distribution curves (SFD, $dM/dH$ of the demagnetization curves) of Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ nanotubes calcined at 700 °C. Essentially, the switching field distribution played a crucial role in
describing the microscopic and uniform properties of the magnetic recording materials. Generally, the direct coupling among the hard materials without any soft magnetic phase could affect the magnetization of the magnetic material, which would be reduced with the increasing hard magnetic phase. In this study, the switching field distribution shows one single peak for Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ samples when $x \leq 0.02$, indicating that there is one step completion of magnetic reversal. It can be seen from figure 8 curves, the appearance of more than two peaks exhibits the weaker exchange coupling with increasing of Cr content [34]. The intensities of the distribution main peaks decreases with the increasing of Cr content, which indicates that the exchange coupling gradually weakened. The switching field curves were shifted to left and the full width at half maximum (FWHM) of the strongest peak decreased with the increasing of Cr content. As illustrated in figure 8 that the single peak was observed from the switching field curves when the Cr content was low ($x < 0.04$) or none ($x = 0$). With increasing of Cr content, different peaks originated from different magnetic phase were observed, which exhibited the magnetically crystal softer phase. Furthermore, the presence of different peaks in the switching field curves indicate that there were multiple-step processes to reach magnetic reversal in the hard magnetic phase [34] ($x > 0.04$).

4. Conclusion

Series of Co$_{1-x}$Cr$_x$Fe$_2$O$_4$ ($x = 0.0, 0.02, 0.04, 0.06, 0.08, 0.1$) were prepared by the electrospinning method and the effect of the Cr substitution on the structure and magnetic properties was studied. The XRD analysis confirmed the formation of the single cubic spinel phase without any oxides impurities. M-H hysteresis loops indicated a slight decrease in the saturation magnetization (Ms) with the increasing Cr content, which could be stemmed from the influence of A-A and A-B interactions combined with the distribution of 3d electrons direction of Cr and Fe cations. Furthermore, the values of remanent magnetization (Mr) and coercivity (Hc) were increased first and then decreased with the Cr content, which were associated with the surface effect and magnetic anisotropy. XPS analysis revealed the Cr cations doped successfully and changed the structure of CoFe$_2$O$_4$ nanotubes. Last but not lease, through the analysis of switching field distribution, the intensity was decreased with the increasing Cr content, which exhibited the weaker exchange coupling, even for nanotubes with the Cr content of up to $x = 0.1$. The results reported in this work are fundamentally important, which would play a crucial role in further improving the performance of the magnetic recording materials.

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