Effect of heat treatment on structure and magnetic properties of FeCoNi/CNTs nanocomposites

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Abstract. Fe₄₆Co₃₅Ni₁₉/CNTs nanocomposites have been prepared by an easy two-step route including adsorption and heat treatment processes. We investigated the effect of heat treatment conditions on structure, morphology, nanoparticle sizes and magnetic properties of the Fe₄₆Co₃₅Ni₁₉ alloy nanoparticles attached on the carbon nanotubes by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), energy-disperse X-ray spectroscopy (EDS) and vibrating sample magnetometer (VSM). When the reducing temperature changes from 300–450°C, a transition of the crystal-line structure from *bcc* phase to *fcc*–*bcc* dual phase and an increase in particle size of Fe₄₆Co₃₅Ni₁₉ nanoparticles together with a local maximum at 350°C are observed. Meanwhile, the saturation magnetization (M_s) for Fe₄₆Co₃₅Ni₁₉ nanoparticles increases with the increase of reducing temperature and the coercivity (H_c) decreases rapidly with a local minimum at 350°C. When the reducing time (tr) changes from 2–5 h, *bcc* phase is predominant in the Fe₄₆Co₃₅Ni₁₉ alloy particles. Both the particle size and M_s have a maximum at $tr = 3$ h, and the H_c reaches a maximum at $tr = 4$ h.

Keywords. Carbon nanotubes; FeCoNi alloy; structure; magnetic properties; heat treatment.

1. Introduction

Metal-coated carbon nanotubes (CNTs) is becoming a promising and challenging area of research owing to their unique applications such as nanoelectronic devices (Dai *et al* 1996), support media in heterogeneous catalysis (Coq *et al* 1998; Liu *et al* 2001), fuel cells (Che *et al* 1999; Steigerwalt *et al* 2002), and magnetic recording (Liu *et al* 2003). As is well known, there have been many reports on the deposition of monometal nanoparticles onto CNTs (Chen *et al* 2005, 2007; Li *et al* 2005; Ayala *et al* 2006; Zheng *et al* 2006; Bittencourt *et al* 2007). As for bimetallic systems or alloys, some reports have appeared (Rajesh *et al* 2000; Chen *et al* 2004; Shi *et al* 2006; Li *et al* 2007). But for ternary metal alloys attached on CNTs, no report is available.

The FeCoNi alloys, which exhibit excellent soft magnetic properties and good thermal stability, have been an interesting research topic (Osaka *et al* 1999, 2005; Saito *et al* 1999; Liu and Zangari 2000; Bai *et al* 2003; Park *et al* 2006). Because of these unusual magnetic properties, the alloys will be widely used for sensor, actuators and magnetic recording. However, it has been seen in many systems that slight variation of the heat treatment condi-

tion can cause substantial change in the structure and magnetic properties. Therefore, the control of heat treatment conditions is often a key element in optimizing the magnetic properties in a magnetic material. The lubricating properties of the graphite coating might be helpful in magnetic recording applications and reinforce the material's durability. Therefore, ternary FeCoNi alloy nanoparticles attached on carbon nanotubes will be a new type of merged giant-magneto-resistive materials, which is considered in the ultra high-density magnetic recording and magnetic storage applications. Here, we have prepared Fe₄₆Co₃₅Ni₁₉ alloy nanoparticles supported on the outer surface of CNTs with fixed composition by an easy two-step route including adsorption and heat treatment processes, and investigated the effects of the reducing temperature and time on the structure and magnetic properties of the alloy nanoparticles.

2. Experimental

The multi-walled carbon nanotubes (MWCNTs) with a purity of about 95% were provided by Shenzhen Nanoport Company, which was produced via catalytic decomposition of hydrocarbon. For the better anchoring of the metal particles, the MWCNTs were treated with boiling HNO₃ (68%, 40 ml) for 4 h. The main procedure employed by us for fabricating Fe₄₆Co₃₅Ni₁₉/CNTs nanocomposites was as follows. The acid-treated CNTs (73.7 mg) were uni-

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formly dispersed in the mixed solution of ferric, cobalt and nickel nitrate which contained $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (106.6 mg), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (58.4 mg), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (31.7 mg) (i.e. the molar ratio of Fe : Co : Ni is 46 : 35 : 19) by ultrasound, followed by stirring for 2 h at room temperature and then strongly stirred at 100°C until the solvent was evaporated completely. The samples were calcined under an argon atmosphere for 3 h, and subjected to reducing treatment in a hydrogen atmosphere at various temperatures for different time from 2 to 5 h, then cooled naturally to room temperature. The reducing temperature ranged from 300–450°C.

X-ray powder diffraction (XRD) was carried out on an XRD-6000 (Japan) X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154060 \text{ nm}$) at a scanning rate of $0.05^\circ \cdot \text{s}^{-1}$ in the 2θ range from 20° to 100° . Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 scanning electron microscope, with an accelerating voltage of 5 kV. High-resolution transmission electron microscopy (HRTEM) was performed using JEM 2010 F field emission microscope operated at optimum defocus with an accelerating voltage of 200 kV. Energy-dispersive X-ray spectrometry (EDS) was carried out with a spectroscope attached to HRTEM, which was used for compositional analysis. Magnetic properties were measured at room temperature by a vibrating sample magnetometer (VSM, Japan BHV-55).

3. Results and discussion

3.1 Structural properties

3.1a Effect of reducing temperature: Figure 1 shows the XRD patterns of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}/\text{CNTs}$ nanocompo-

Figure 1. XRD patterns of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}/\text{CNTs}$ nanocomposite reduced at different temperatures for 4 h.

sites reduced at different temperatures for 4 h. A transition of the crystalline structure from *bcc* phase to *fcc*–*bcc* dual phase was observed with increasing reducing temperature (T_r). When $T_r = 300^\circ\text{C}$, 350°C , the alloy is characterized by body centred cubic (*bcc*) phase and *bcc* (110) is predominant. However, when $T_r = 400^\circ\text{C}$, 450°C , the face centred cubic (*fcc*) phase coexists obviously in the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles and *bcc* (110) is still predominant.

The mean crystalline sizes of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles were investigated with different T_r from the widths of the major *bcc* (110) peak observed in figure 1 using Debye–Scherrer formula. The experimental results are listed in table 1. It can be seen that the mean crystalline size of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles increases with increasing T_r together with a local maximum at 350°C . However, there is an abrupt decrease from 350 – 400°C , which may be caused by the appearance of the *fcc* phase. In general, the grain size for *fcc*–*bcc* biphasic particles is smaller than that for *fcc* or *bcc* particles (Nam et al 2001; Liu et al 2003).

Figure 2. SEM images of $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles attached on CNTs reduced for 4 h at (a) 350°C and (b) 400°C .

Table 1. The mean crystalline sizes, D and room-temperature magnetization data of Fe₄₆Co₃₅Ni₁₉ alloy nanoparticles attached on CNTs vs reducing temperature.

Reducing temperature (°C)	300	350	400	450
D (nm)	15.7	22.4	17.7	26.9
Actual (Fe:Co:Ni)	38.5 : 44.2 : 17.4	46.1 : 32.8 : 21.1	50.2 : 30.7 : 19.1	46.6 : 34.4 : 19
M_s (emu/g of FeCoNi)	99.1	133.8	132.0	191.6
H_c (Oe)	983.7	448.2	618.2	471.9

Figure 3. (a) HRTEM image and (b) selected area electron diffraction (SAED) pattern of Fe₄₆Co₃₅Ni₁₉ alloy nanoparticles attached on CNTs reduced at 400°C for 4 h.

The SEM images of the Fe₄₆Co₃₅Ni₁₉/CNTs nanocomposites reduced at different T_r are shown in figure 2. The

Figure 4. EDS spectrum of the Fe₄₆Co₃₅Ni₁₉/CNTs nanocomposite reduced at 400°C for 4 h. **Figure 5.** XRD patterns of the Fe₄₆Co₃₅Ni₁₉/CNTs nanocomposite reduced at 400°C for different times.

FeCoNi alloy nanoparticles are quasi-spherical attached on the surface of the CNTs. High-resolution TEM observation (figure 3a) shows lattice fringes with observed fringe separations of ca. 2.06 and 2.03 Å, consistent with the interlayer separations of the (111) crystal plane of *fcc* and (110) of *bcc* for Fe₄₆Co₃₅Ni₁₉ attached on CNTs. The SAED pattern (figure 3b) shows the diffraction rings (the

Table 2. The mean crystalline sizes, D and room-temperature magnetization data of $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles attached on CNTs vs reducing time.

Reducing time (h)	2	3	4	5
D (nm)	15.2	29.9	17.7	20.8
Actual (Fe:Co:Ni)	44.4:33.1:22.4	46.1:32.8:21.1	50.2:30.7:19.1	43.8:35.1:21.1
M_s (emu/g of FeCoNi)	136.7	175.2	132.0	132.7
H_c (Oe)	527.7	531.9	618.2	523.5

Figure 6. SEM images of $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles attached on CNTs reduced at 400°C for (a) 2 h and (b) 3 h.

smallest ring is the diffraction ring of CNTs) due to *fcc* (111) and *bcc* (110) planes and that the alloy is multicrystal. These results verify further that the particles reduced at 400°C are *fcc*–*bcc* dual phase.

The chemical composition of the alloy nanoparticles attached on the CNTs was analysed using the EDS spectrometer attached to the high-resolution electron microscope. The EDS spectrum of an individual nanoparticle shows that the sample contains carbon, iron, cobalt and copper. Figure 4 is shown as an example. It is obvious that the copper peak is caused by the copper grid holding the sample, and the carbon peaks are present from the CNTs.

EDS quantitative microanalysis indicates the composition of Fe (46.91 at.%), Co (35.95 at.%) and Ni (17.14 at.%) in $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ (reduced at 400°C for 4 h). It was noted that the composition of FeCoNi alloy attached on the surface of CNTs had a slight departure. Fortunately, the alloy composition was close to the original composition of nitrates.

3.1b Effect of reducing time: The X-ray diffraction of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ /CNTs nanocomposites reduced at 400°C for different time (tr) is shown in figure 5. The X-ray diffraction peak at 26.00° is attributed to the CNTs (002). Other peaks show that *bcc* phase is predominant in the alloy particles of all samples. The mean crystalline sizes of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles were investigated with different reducing times from the widths of the major *bcc* (110) peak observed in figure 5 using Debye–Scherrer formula. The mean crystalline sizes of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles increase from 15.2 to 20.8 nm with reducing time except for the sample reduced for 3 h having an abrupt increase in the particle size as shown in table 2. The abrupt increase may result from the high crystallinity of the alloy particles. As shown in figure 5, the relative intensity of *bcc* (110) peak for the sample reduced for 3 h is the biggest, which is probably due to the high crystallinity of the nanoparticles.

The SEM images of the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ /CNTs nanocomposites reduced for different tr are shown in figure 6. The $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy nanoparticles are quasi-spherical attached on the surface of the CNTs. For the sample reduced for 3 h, most alloy nanoparticles are relatively large.

3.2 Magnetic measurement

3.2a Magnetic properties of $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ /CNTs nanocomposites versus reducing temperature: Magnetic properties of the samples were investigated at room temperature using a vibrating sample magnetometer with an applied field of $-10000 \text{ Oe} \leq H \leq 10000 \text{ Oe}$. Figure 7 showed the hysteresis loops of $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ /CNTs nanocomposites reduced at different temperatures for 4 h. Table 1 shows the saturation magnetization (M_s) and coercivity (H_c) for all samples as a function of reducing temperature. It can be seen that the M_s increases with the increase of reducing temperature and H_c decreases rapidly with a

local minimum at 350°C. This change in behaviour of H_c can be related to the crystalline size. According to the theory of magnetic domain (Tang *et al* 2002), if the magnetic particles (D) are large enough to have multiple domains (where D is larger than the critical size, d_s , of single domain particles), magnetization of ferromagnetic materials occurs via domain wall movement; the coercivity decreases as grain size increases. However, if the grain size is smaller than d_s (where the magnetic particles are the single-domain particles for the principle of minimum energy), the coercivity increases with the increase of the grain size (Yoo *et al* 2006). Thus the H_c shows the maximum when D is equal to d_s (Tang *et al* 2002).

Figure 7. Room-temperature hysteresis loops of Fe₄₆Co₃₅Ni₁₉ alloy attached on CNTs reduced at different temperatures for 4 h.

Figure 8. Room-temperature hysteresis loops of Fe₄₆Co₃₅Ni₁₉ alloy attached on CNTs reduced at 400°C for different times.

The particle size increases with the increase of the reducing temperature. When the reducing temperature is higher than 300°C, the ratio of multi-domain particles increases and the domain wall movement controls the magnetization process. As a result, the H_c decreases. On the other hand, the dramatic decrease of H_c with reducing temperature may be caused by the reduction of the internal stress. The local minimum of the H_c at $T_r = 350^\circ\text{C}$ is caused by the large size of the particle. The highest coercivity value is observed at 300°C. High coercivity for the Fe₄₆Co₃₅Ni₁₉ alloy nanoparticles reduced at 300°C is related to following factors: disordered structure and small nanoparticle size. For equiatomic FeCo alloy, the K_1 value for ordered structure is negligibly small, whereas the disordered alloy exhibits a relatively large negative K_1 , resulting in a higher H_c for the disordered sample. This disordered structure is unstable and will transform to the ordered phase at high temperature (Yu *et al* 1999).

The M_s increases with the increase of reducing temperature. The change in behaviour of M_s is similar to the result reported in the literature (Tang *et al* 2002), which may be caused by the alloy content and high crystallinity. As shown in figure 1, the relative intensity of the Fe₄₆Co₃₅Ni₁₉ alloy (110) peak increases gradually with increasing reducing temperatures, which is probably due to the loss of CNTs in weight on heat treatment and increasing high crystallinity of the nanoparticles.

3.2b Magnetic properties of Fe₄₆Co₃₅Ni₁₉/CNTs vs reducing time: Figure 8 shows the hysteresis loops of Fe₄₆Co₃₅Ni₁₉/CNTs reduced at 400°C for different times. The effect of reducing time (tr) on the magnetic properties of the Fe₄₆Co₃₅Ni₁₉/CNTs samples reduced at 400°C is shown in table 2. It can be seen that the H_c increases when tr changes from 2 to 4 h and decreases as the reducing time increases further, which is consistent with the reported result (Tang *et al* 2002). These experimental findings may result from the change of the particle size and crystallinity of the Fe₄₆Co₃₅Ni₁₉ alloy with the reducing time. When tr increases from 2 to 4 h, the particle size increases, having a local maximum at $tr = 3$ h. When $tr = 4$ h, the mean particle size is close to the critical size d_s . As a result, H_c increases in this range and gets its maximum at $tr = 4$ h. When $tr > 4$ h, the multi-domain particles are predominant. Therefore, H_c decreases.

The M_s does not vary with reducing time greatly except for the sample reduced for 3 h having an abrupt increase in the saturation magnetization value, which may result from the high crystallinity of the alloy particles as shown in figure 5.

4. Conclusions

We have prepared Fe₄₆Co₃₅Ni₁₉/CNTs nanocomposites by an easy two-step route including adsorption and heat treat-

ment processes. The nanoparticles are quasi-spherical and disperse disorderly on the surface of CNTs. When the heat treatment condition changes, the particle size of $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ nanoparticles increases with increasing reducing temperature together with a local maximum at 350°C and increases from 15.2 to 20.8 nm with reducing time except for the sample reduced for 3 h having an abrupt increase in the particle size. When the reducing time (tr) changes from 2 to 5 h, bcc phase is predominant in the $\text{Fe}_{46}\text{Co}_{35}\text{Ni}_{19}$ alloy particles. The samples reduced at 400 and 450°C are fcc - bcc dual phase. The M_s and H_c vary with heat treatment condition. The M_s for FeCoNi nanoparticles increases with increasing temperature and H_c decreases rapidly with a local minimum at 350°C . And the M_s have a maximum at $tr = 3$ h, and the H_c reaches a maximum at $tr = 4$ h.

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