Synthesis of high saturation magnetization FeCo nanoparticles by polyol reduction method

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ABSTRACT

FeCo nanoparticles with different compositions were prepared by a polyol reduction method and annealed in gas mixtures. All FeCo nanoparticles show large saturation magnetization (over 220 emu/g). The largest saturation magnetization of 273 emu/g was observed in the Fe₅₅Co₄₅ sample. As for Fe₄₈Co₅₂, the impurity phase of CoFe₂O₄ existed when nanoparticles were annealed at low temperature (200 to 400 °C). While annealed at above 450 °C, pure Fe₄₈Co₅₂ nanoparticles with large saturation magnetization of 230 emu/g were obtained. These FeCo nanoparticles with large saturation magnetization have great potential in some industry fields.

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1. Introduction

Magnetic nanoparticles with high saturation magnetization (M_s) have attracted wide attention due to their great potential in data storage, magnetic separation, drug delivery and imaging applications [1,2]. For example, magnetic nanoparticles used in hyperthermia and targeted drug delivery require high M_s for their easy manipulation through magnetic field assistance. Furthermore, magnetic nanoparticles with high M_s have been developed for magnetic resonance imaging contrast enhancement [3]. Similarly, for biosensor application, high magnetic moments are required for efficient shift of the functionalized labels to the specific sensor sites [4,5].

FeCo based nanoparticles have got much attention due to their high M_s , large permeability, low coercivity (H_c), and high Curie temperature [6,7]. FeCo based nanoparticles have been prepared through several methods, such as sol-gel method [8], electrochemical deposition [9], magnetron sputtering [10], thermal decomposition [11], chemical vapor deposition [12]. However, there are some limitations including complex synthesis process, long synthesis duration, use of environmentally harmful chemicals, high production cost. Compared with these methods, polyol process is a simple, environmental friendly, easy control of experimental parameters and low cost method [5,13]. Polyols act as reducing agent also overcomes the problem of oxidation of metal particles in solution.

In this work, FeCo nanoparticles with different composition were prepared by a polyol reduction method and followed by annealing in reductive atmosphere. The obtained FeCo nanoparticles show satisfactory microstructure and high M_s .

2. Materials and methods

In a typical synthesis procedure, FeCo particles with different composition were prepared

by using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, NaOH and ethylene glycol. The concentration of metal salts was fixed at 0.05 mol/L and the Fe/Co molar ratio was varied according to the anticipated composition. Then a certain amount of NaOH was added to provide an alkaline environment. The mixed solution was subsequently ultrasonicated for 5 minutes and heated to 130 °C for 3h in an erlenmeyer flask. After that, the black precipitation at the flask bottom was collected with a magnet and ultrasonic washed several times using ethanol and water. Finally, the cleaned black particles were annealed in 90% Ar and 10% H_2 mixed gas.

The composition of the particles was analyzed by x-ray fluorescence (XRF-1800) instrument and energy dispersive x-ray spectroscopy (EDX) fitted to a scanning electron microscopy (SEM). The morphology of the particles was analyzed by using SEM (JSM 7100). The crystal structure was determined by x-ray diffraction (XRD, Bruker D8) and the magnetic properties were measured at room temperature using a vibrating sample magnetometer (VSM, LakeShore model 7400).

3. Results and discussion

Fig. 1. The XRD patterns of FeCo nanoparticles with different Fe、Co composition annealed at 850 °C for 5 h.

Figure 1 shows the XRD patterns of FeCo nanoparticles with different composition annealed at 850 °C for 5 h. It can be seen that no impurity phases are detected, and all diffraction peaks can be indexed corresponding to the standard JCPDS data for FeCo (No:

49-1567), indicating the formation of single phase FeCo. Furthermore, all the diffraction peaks shifted slightly towards lower angle with increasing Fe composition. This is caused by the substitution of Fe atoms with larger atomic radius for Co atoms with smaller atomic radius, which would induce the expansion of the FeCo unit cell.

Fig. 2. The room temperature hysteresis loops of FeCo nanoparticles annealed at 850 °C for 5 h with different Fe, Co composition. Inset: the composition dependence of M_s and H_c in FeCo nanoparticles.

Figure 2 shows the room temperature hysteresis loops of FeCo nanoparticles with different compositions annealed at 850 °C for 5 h. The inset shows the dependence of M_s and H_c on the composition of FeCo nanoparticles. The M_s of all FeCo nanoparticles is over 220 emu/g. In Fe₅₅Co₄₅ sample, we have obtained the M_s of 273 emu/g. Although the value is smaller than the theoretical prediction [14], it is larger than the previously reported values until now [13]. Among all the samples, the samples with high cobalt content (over 50%) show smaller M_s which might be attributed to the higher magnetic moment of Fe compared with Co. Besides, the lowest H_c of 82 Oe was observed in the Fe₄₈Co₅₂ sample, which is due to much more pure FeCo samples and less impurities and defects. The existence of impurities and defects will act as pinning sites to enhance the coercivity and decrease the magnetic anisotropy energy. The magneto-crystalline anisotropy was reported to be compositionally dependent and would reach its maximum in a little more Co-rich FeCo samples [14, 15].

The XRD patterns of Fe₄₈Co₅₂ nanoparticles annealed at different temperatures for 5 h are

shown in Fig. 3. When annealed at 200 °C and 350 °C, except obvious reflections belonging to FeCo, the peaks at 30.1°, 35.4°, 57° and 62.6° corresponding to (220), (311), (511) and (440) reflections of CoFe_2O_4 are present. The appearance of CoFe_2O_4 might be attributed to the partially oxidation of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles. With increasing annealing temperature (T_a) to 400 °C, the intensity of the (311), (440) peaks decrease and the (220), (511) peaks disappear. With further increasing T_a to 450 °C, all of the CoFe_2O_4 reflections vanished and only FeCo diffraction peaks were observed.

Fig. 3. The XRD patterns of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles annealed at different temperatures from 200 to 850 °C for 5 h.

Fig. 4. The SEM images of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles annealed at (a) 300 °C (b) 400 °C (c) 450 °C (d) 500 °C.

The SEM images of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles with different T_a ranging from 300 °C to 500 °C are shown in Fig. 4. When annealed at low temperature (300 °C and 400 °C), small and uniform particles were observed. The average particle size was estimated to be about 40 nm.

When increasing T_a to 450 °C, the average particle size increased sharply from about 40 nm to about 100 nm. The formation of large particles might be due to the aggregation of small particles, which is induced by the strong magnetic interaction between FeCo grains [16]. When further increasing T_a to 500 °C, much larger particles were observed because of the growth of the grains and more aggregation of small particles.

Fig. 5. The room temperature hysteresis loops of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles annealed at different temperatures for 5 h. Inset: the T_a dependence of M_s and H_c in $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles.

Figure 5 shows the room temperature hysteresis loops of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles annealed at different temperatures for 5 h. The inset shows the dependence of M_s and H_c on T_a in $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles. It can be seen that the M_s of $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles increases rapidly with increasing T_a from 200 °C to 400 °C. The sharp increase of M_s is due to the reduction of CoFe_2O_4 and more complete phase transformation. When $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles were annealed at 450 °C, large M_s of 230 emu/g was obtained. With further increasing T_a , the M_s has little change which might be attributed to the finish of phase transformation. Furthermore, we can find that the H_c increases firstly and then decreases with increasing T_a . The maximum $H_c \sim 203$ Oe was obtained when T_a is 400 °C. When annealed at below 400 °C, $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles might be in a single-domain state because of small particle size indicated in Fig. 4(a) and (b), and the magnetization reversal occurs by rotation of all the magnetic moment which requires the anisotropy energy to be dominated. With increasing T_a to 450 °C, the

multidomain state is favored since the size of particles increase, as shown in Fig. 4(c) and (d), and the magnetization is changed to the movement of domain walls. Since the anisotropy energy is much higher than domain wall energy, the H_c increases to the maximum value when T_a is 400 °C and then decreases because the formation of multidomain nanoparticles in FeCo samples [17].

4. Conclusions

In summary, FeCo nanoparticles with different compositions were prepared by a polyol reduction method. When annealed at 850 °C for 5 h, all FeCo nanoparticles with Fe atomic concentration ranging from 29% to 65% show large M_s (over 220 emu/g). The largest M_s of 273 emu/g and the lowest H_c of 82 Oe were obtained in Fe₅₅Co₄₅ and Fe₄₈Co₅₂ nanoparticles respectively.

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Reference

- [1] N.A. Frey, S. Peng, K. Cheng, S.H. Sun, Chem. Soc. Rev. 38 (2009) 2532.
- [2] T.L. Doane, C. Burda, Chem. Soc. Rev. 41 (2012) 2885.
- [3] W.S. Seo, J.H. Lee, X.M. Sun, Y. Suzuki, D. Mann, Z. Liu, M. Terashima, P.C. Yang, M.V. McConnell, D.G. Nishimura, H.J. Dai, Nature Mater. 5 (2006) 971.
- [4] E.P. Furlani, K.C. Ng, Phy. Rev. E. 73 (2006) 061919.
- [5] R.J. Joseyphus, K. Shinoda, D. Kodama, B. Jeyadevan, Mater. Chem. Phys. 123 (2010) 487.
- [6] D. Kodama, K. Shinoda, K. Sato, Y. Konno, R.J. Joseyphus, K. Motomiya, H. Takahashi, T. Matsumoto, Y. Sato, K. Tohji, B. Jeyadevan, Adv. Mater. 18 (2006) 3154.
- [7] C. Desvaux, C. Amiens, P. Fejes, P. Renaud, M. Respaud, P. Lecante, E. Snoeck, B. Chaudret, Nature Mater. 4 (2005) 750.
- [8] G. Ennas, A. Falqui, S. Marras, C. Sangregorio, G. Marongiu, Chem. Mater. 16 (2004) 5659.
- [9] C.W. Qiang, J.C. Xu, S.T. Xiao, Y.J. Jiao, Z.Q. Zhang, Y. Liu, L.L. Tian, Z.G. Zhou, Appl. Surf. Sci. 257 (2010) 1371.
- [10] S. Li, Z. Huang, J.G. Duh, M. Yamaguchi, Appl. Phys. Lett. 92 (2008) 092501.
- [11] V. Tzitzios, G. Basina, D. Niarchos, W.F. Li, G. Hadjipanayis, J. Appl. Phys. 109 (2011) 07A313.
- [12] D. Hisada, Y. Fujiwara, H. Sato, M. Jimbo, T. Kobayashi, K. Hata, J. Magn. Magn. Mater. 323 (2011) 3184.
- [13] M. Abbas, M.N. Islam, B.P. Rao, T. Ogawa, M. Takahashi, C.G. Kim, Mater. Lett. 91 (2013) 326.
- [14] G. Moulas, A. Lehnert, S. Rusponi, J. Zabloudil, C. Etz, S. Ouazi, M. Etzkorn, P. Bencok, P. Gambardella, P. Weinberger, H. Brune, Phys. Rev. B 78 (2008) 214424.
- [15] G. Andersson, T. Burkert, P. Warnicke, M. Björck, B. Sanyal, C. Chacon, C. Zlotea, L.

Nordström, P. Nordblad, O. Eriksson, Phys. Rev. Lett. 96 (2006) 037205.

[16] J.M. MacLaren, T.C. Schulthess, W.H. Butler, R. Sutton, M. McHenry, J. Appl. Phys. 85 (1999) 4833.

[17] M. Hesani, A. Yazdani, B. Abedi Ravan, M. Ghazanfari, Solid State Commun. 150 (2010) 594.