CONDENSED MATTER: ELECTRONIC STRUCTURE, ELECTRICAL, MAGNETIC, AND OPTICAL PROPERTIES

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Fabrication and Mössbauer Study of FeCo Alloy Nanotube Array *

ZHOU Dong(周栋), LI Zhi-Wei(李志伟), YANG Xu(杨旭), WEN Fu-Sheng(温福昇), LI Fa-Shen(李发伸)**

Institute of Applied Magnetics, Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000

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Arrays of FeCo nanotubes are fabricated in the pores of porous anodic aluminium oxide templates. Transmission electron microscopic result shows that the nanotubes are regular and uniform. Magnetic hysteresis loops measured at room temperature are different from those of nanowires with the same composition, which are caused by the unique shape of nanotubes. The Mössbauer spectra show that the hyperfine field is smaller than that of the bulk's and increases with decrease of measuring temperature. However, the areas of the doublets appeared in Mössbauer spectra decrease with decrease of measuring temperature.

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FeCo bulk alloys are important magnetic materials due to both high saturation magnetization and Curie temperature, parameters that cannot be matched by any other alloy system. FeCo alloys are mainly used as soft magnetic materials.[1] Research on FeCo nanoparticles,[2] nanowires,[3,4] and ultrathin films has plenty of outcomes.[5] Research on tubular nanostructure is an important aspect of magnetic nanotechnology. Previous studies demonstrated the potential applications of magnetic metal nanotubes in nanomedicine and biotechnology,[6] ultrahigh-density magnetic storage devices,[7] nanoelectromechanical system device,[8] and nanotube-based multilayer nanostructure.[9] Fabrication and magnetic properties of nanotubes based on FeCo alloys have few reports so far.

Anodic aluminium oxide (AAO) templates with a pore diameter of about 200 nm were prepared under conventional two-step anodizing process.[10] After that, FeCo nanotube arrays were fabricated according to the following steps. Step 1: The AAO templates were dipped into a solution of $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ with a molar ratio of about 2:1. Step 2: The loaded templates were cleaned and then fixed on a sample holder, with pores mounted horizontally, and dried in an oven at 60°C for more than 10 h. Then a thin Co/Fe nitrate film covered the pore wall. Step 3: The templates were placed in an oven for 3 h at 400°C for decomposition of the metal salts. Step 4: The samples were put into an oven with flowing hydrogen for 3 h at 350°C to form FeCo nanotube arrays. Steps 1–3 can be repeated again and again, so the thickness and quality of tube wall can be changed. By varying the number of dips, samples with different tube wall thickness can be prepared. For convenience of the fabrication, four times of the dip-coating procedure will be a good choice.

After the nanotube array was formed, it was etched in 0.1 M NaOH solution. The precipitates were dispersed in ethanol for transmission electron microscopy (TEM) observation. The transmission Mössbauer spectroscopy measurements were performed with the γ-ray beam parallel to the nanotube axis. The γ-ray source of the Mössbauer spectrometer is 25 mCi ^{57}Co in Pd. Using α-Fe to calibrate the driver velocity, the hyperfine parameters were calculated by fitting Lorentzian line shapes to the experimental data using the least-squares method. The magnetic properties over the temperature range of 10–300 K were measured by a quantum design magnetometer (MPMS XL SQUID).

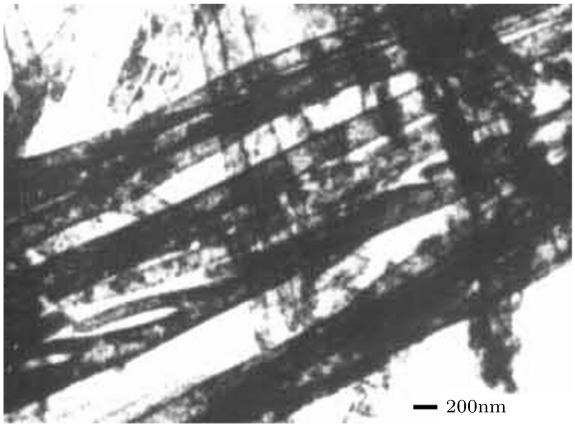

Fig. 1. TEM image of a bunch of FeCo nanotubes with 200 nm in diameter.

Figure 1 shows the TEM image of FeCo nanotubes released from alumina template. The average diameter is about 200 nm, and the length is more than 10 μm. Figure 2 shows the hysteresis loops of the FeCo alloy nanotube array, measured at 300 K, where $H_{\parallel}$ and $H_{\perp}$ indicate that the applied fields are parallel

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**Email: lifs@lzu.edu.cn

and perpendicular to the nanotube axis, respectively. It is found that the coercivities Hc for $H_{\parallel}$ and $H_{\perp}$ are 955 Oe and 886 Oe, respectively; the remanence ratio for $H_{\parallel}$ and $H_{\perp}$ are 0.51 and 0.34, respectively. The results indicate that, when the external magnetic field is parallel to the tube axis, the FeCo nanotube array could be magnetized more easily. Our group has studied the variety of the coercivity of FeCo alloy nanowire in a previous report,[3] from which we can find that the anisotropy of the FeCo nanotube is much weaker than that of FeCo nanowire.

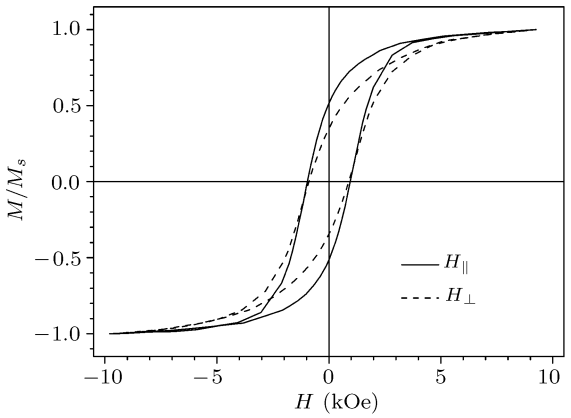

Fig. 2. Hysteresis loops of FeCo alloy nanotube array at room temperature. $H_{\parallel}$ and $H_{\perp}$ represent that the applied fields are parallel and perpendicular to the tubes axis.

In order to study the microscopic magnetic properties deeply, Mössbauer spectra of the FeCo nanotube array with AAO template were recorded at 83 K, 133 K, 183 K and 288 K. Figure 3 shows the Mössbauer spectra measured at different temperatures, from which we can find that all of the four spectra can be fitted by a magnetic splitting sextet and a paramagnetic doublet.

In the Mössbauer spectra, the intensity ratio of 2, 5 peaks and 1, 6 peaks ($I_{2,5}/I_{1,6}$) depends on the angle between the γ beam and magnetic moments in the sample, and can be written as[11]

$$I_{2,5}/I_{1,6} = 4\sin^2\theta/3(1+\cos^2\theta), \qquad (1)$$

when $\theta = 0°$, the intensity ratio $I_{2,5}/I_{1,6}$ is 0, and $I_{2,5}/I_{1,6}$ is 4/3 when $\theta = 90°$. If the distribution of magnetic moments is spatially isotropic, $I_{2,5}/I_{1,6}$ is 2/3. For FeCo nanowires with the same composition, the 2 and 5 peaks in the sextet almost disappear, which indicates that the direction of the magnetic moments is parallel to the nanowires.[4] From Fig. 3, the relative intensity ratios $I_{2,5}/I_{1,6}$ in all the spectra are near 2/3, which indicates that the distribution of magnetic moments in the nanotube array is spatially isotropic. Compared with the one-dimensional (1D) nanowire and zero-dimensional (0D) particle, the quasi-1D nanotube has its own unique magnetic properties. For the nanowire arrays and particles, magnetic moments lie predominately along the long axis of wire and are spatially isotropic, in order to minimize the demagnetization energy.[2−4] However the spatially isotropic property of the magnetic moment in the nanotube is different from that of the particle, as shown in our previous report.[12]

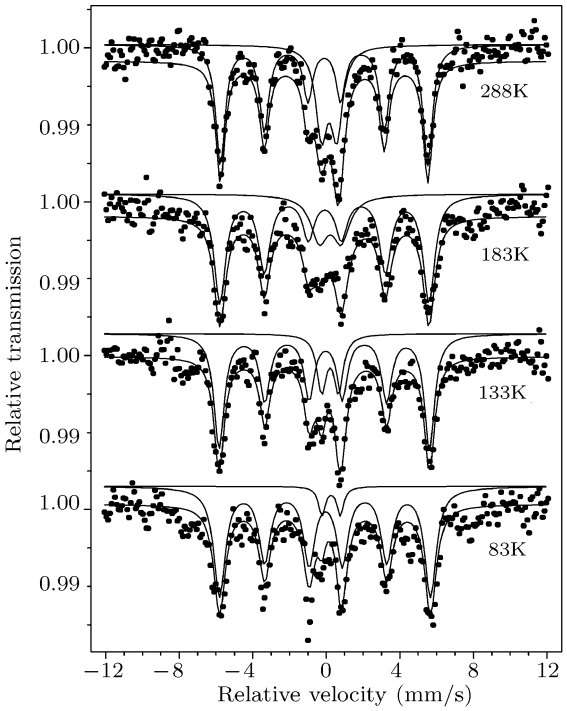

Fig. 3. Thermal variation of Mössbauer spectra for FeCo nanotube array with AAO template.

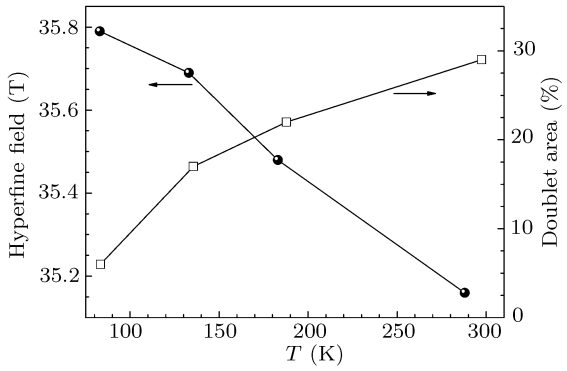

Fig. 4. Hyperfine field and doublet area of the FeCo nanotube array with AAO template as a function of measuring temperature.

The hyperfine field and the area of the paramagnetic doublet deduced from the Mössbauer spectra are shown in Fig. 4. The hyperfine field is 35.2 T at 288 K, which is smaller than that of the bulk, nanowire and particle of the same composition.[2,4] As can be seen from Fig. 4, the hyperfine field is reduced with the increase of measuring temperature. These can be ex-

plained by the collective magnetic excitations.[13] In this theory, the magnetic moments of small size grains fluctuate around an equilibrium position because of thermal disturbances and then the average hyperfine magnetic field can be expressed as

$$H_{hf}(V,T) = H_{hf}(V=\infty,T)\langle\cos\theta\rangle_T, \quad (2)$$

$$\langle\cos\theta\rangle_T \approx 1 - k_B T/2\,KV, \quad (3)$$

where $H_{hf}(V=\infty,T)$ is of the bulk sample, V is the volume of a particle, $\langle\cos\theta\rangle_T$ is the average cosine value of the angle between the magnetization and the easy magnetizing axis; k_B is Boltzmann's constant, and K is the effective anisotropy constant of the particle. From the above equations, the variation of hyperfine field showed in Fig. 4 can be understood.

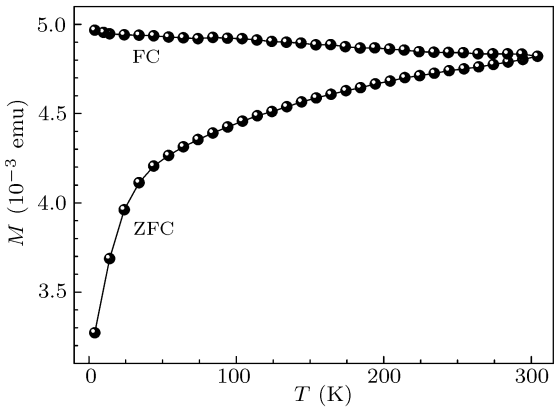

Fig. 5. ZFC and FC magnetizations as a function of temperature with an applied field of 2000 Oe for FeCo alloy nanotube array.

FeCo nanotubes prepared by this method are composed of nanograins, the coupling of some tube walls is not compact. The doublets shown in Fig. 3 come primarily from superparamagnetic relaxation caused by small size effect. This can be proven by the relation between the doublet area and the measuring temperature. As can be seen from Fig. 4, the area of the doublet is reduced with the decrease of measuring temperature. A superparamagnetic relaxation of the small size grains in the polycrystalline nanotubes is involved in the thermally activated process, by which the doublet is affected. To confirm the deduction, standard zero field cooling (ZFC) and field cooling (FC) curves shown in Fig. 5 were measured between 10 K and 300 K under the applied field of 2000 Oe. ZFC and FC curves are usually used to obtain the information of the energy barriers. As can be seen from Fig. 5, a turning point of the slope of the ZFC curve appears at about 50 K. However, previous research of the FeCo alloy with the same composition shows that the change of slope of the ZFC curve is small.[14] The turning point of the ZFC curve shown in Fig. 5 may be caused by some superparamagnetism nanograins in the sample. From Figs. 4 and 5, we can find that the superparamagnetic part in the sample have a wide grain size distribution. Because of the difference in the characteristic measuring time, the blocking temperatures of the superparamagnetic part in the sample measured by a M?ssbauer spectrometer and an SQUID are different.[15] The measuring time of the Mössbauer spectrometer is much shorter than that of the SQUID, so the blocking temperature measured by Mössbauer spectra is higher than that obtained from the ZFC curve.

In summary, FeCo polycrystalline nanotubes have been prepared within the nanochannels of AAO templates by a simple method. The FeCo nanotube array exhibits magnetic anisotropy, and the easy axis is parallel to the nanotube axis. Based on the results of Mössbauer measurements, the hyperfine field of the FeCo nanotubes is smaller, and the nanotubes fabricated by this method contain some nanograins, some of which could be smaller than the critical size of superparamagnetism.

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