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Fabrication and magnetic properties of Sm_2Co_{17} and Sm_2Co_{17}/Fe_7Co_3 magnetic nanowires via AAO templates

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The Sm_2Co_{17} single-phase and Sm_2Co_{17}/Fe_7Co_3 double-phase nanowire arrays with smaller diameter (around 50 nm) have been fabricated into the anodic aluminum oxide (AAO) templates by direct-current electrodeposition. The crystal structure and micrograph of these nanowire arrays were characterized by X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy (TEM). It is found that the as-deposited Sm_2Co_{17} nanowires have the amorphous microstructure. The magnetic hysteresis loops obtained by vibrating sample magnetometer (VSM) show that the easily magnetized direction of the Sm_2Co_{17} single-phase and Sm_2Co_{17}/Fe_7Co_3 double-phase nanowire arrays is parallel to the nanowire arrays and the exchange coupling interaction in nanocomposite Sm_2Co_{17}/Fe_7Co_3 is discussed. The study of the Sm_2Co_{17} single-phase and Sm_2Co_{17}/Fe_7Co_3 double-phase nanowires with small diameter may open up new opportunities for the design and control of nanostructures such as the fabrication of magnetic recording devices.

1. Introduction

In the last few decades, the nanocomposite magnets of exchange-coupling interaction between magnetically soft and hard grains, which combined the advantages of higher coercive fields and saturation magnetization, have attracted much attention from researchers in this field. Since this kind of nanocomposite magnets plays an important role in advanced data storage and magnetoelectronic applications, they are vigorously investigated both theoretically and experimentally [1–6]. Various multilayered nanowires including $Nd_2Fe_{14}B/Fe_3B$ [7] and $Pr_2Fe_{14}B/\alpha$-Fe [8] have been investigated extensively. However, as far as we know, a few investigations have been published on Sm–Co nanofibers, and especially Sm–Co/Fe–Co nanowire arrays. Recently, some methods have been applied to prepare the nano-materials, such as chemical vapor deposition (CVD), physical vapor deposition (PVD), sol–gel method and electrodeposition with anodic aluminum oxide (AAO) templates. Among them, template synthesis using electrodeposition takes good advantages of low cost and high-output. Our research will make great contributions to the fabrication of Sm–Co and Sm–Co/Fe–Co nanowires by changing experimental conditions. Interests have been shown in the fabrication of Sm_2Co_{17} nanocrystals by annealing amorphous Sm–Co nanowires in an atmosphere of pure Ar.

In this paper, the Sm_2Co_{17} and Sm_2Co_{17}/Fe_7Co_3 magnetic nanowires grown inside the AAO templates by potentiostatic electrochemical deposition have been studied at room temperature, and their magnetic properties are characterized. Furthermore, the morphology, structure and possible grown processes of the self-assembled nanowires are illustrated.

2. Experiment

The AAO templates were prepared by a two-step anodization process as described in detail previously [9]. For convenience, here we only introduce the deposition process of amorphous Sm_2Co_{17} nanowires and Sm_2Co_{17}/Fe_7Co_3 multiple phase nanowire arrays.

In the electrodeposition step, electrolyte concentrations, voltage, temperature and pH value are the significant factors in the growth mechanism of deposited alloy. Low Sm ion concentration and a proper direct current (DC) voltage can facilitate the Sm_2Co_{17} phase growth.

Prior to electrodeposition, an Au film was deposited by vacuum evaporation on one side of each through-hole AAO templates. The AAO/Au substrates (pore diameter $dp \approx 50$ nm and thickness $t \approx 30$ μm) served as the working electrode in a two-electrode potentiostatic control and direct current electrodeposition system with a 4.0 cm × 4.0 cm graphite plate as counter electrode. The Sm_2Co_{17} alloys were electrodeposited from an aqueous bath containing $SmCl_3$, $CoCl_2$, H_3BO_3, HCl, ascorbic acid ($C_6H_8O_6$), and glycine ($NH_2 \cdot CH_2 \cdot COOH$) with the pH value of 2.0. The electrolyte for preparation of Fe_7Co_3 layers contained $FeCl_2$, $CoCl_2$, H_3BO_3, and

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ascorbic acid ($C_6H_8O_6$) with the pH value of 2.5. Ascorbic acid was used as antioxidant and glycine as a complexing agent. The concentrations of the reagents are listed in Table 1. The electrodeposition was carried out at 2.5 V (DC voltage) for Sm_2Co_{17} nanowires, 2.0 V (DC voltage) for Fe_7Co_3 layer of the multiple phase nanowires, respectively. The Sm_2Co_{17}/Fe_7Co_3 multiple phase nanowires were obtained by the dual-bath method to avoid the diffusion between two alloys. After the deposition, the filled AAO templates (Sm_2Co_{17} amorphous nanowires and Sm_2Co_{17}/Fe_7Co_3 multiple phase nanowire arrays) were annealed in a vacuum of 10^{-6} bar or in an argon atmosphere at 660 °C for 4 h before measurements.

The crystal structures of single and multiple phase nanowires were characterized by X-ray diffractometer (XRD) with Cu Kα_1 radiation (λ=0.154056 nm). The morphologies of the AAO template and nanowire arrays were observed with field-emission scanning electron microscopy (FESEM). The atomic percentage of Sm and Co in the nanowires was determined by energy-dispersive X-ray spectroscopy (EDS). Magnetic properties of the nanowire arrays were measured at room temperature using Lake-Shore 7407 series vibration sample magnetometer (VSM).

3. Results and discussion

In order to study the structure of the single-phase and double-phase nanowires, X-ray diffraction was used at first. Fig. 1(a) shows the typical XRD pattern of Sm_2Co_{17} nanowires, from which we can see that no obviously sharp diffraction peak is shown, indicating amorphous-like structure of as-deposited. After annealing at 660 °C for 4 h in 99.99% Ar, the diffraction peaks are found at 30.49°and 62.68°, corresponding to the 101 and 211 planes of hexagonal Sm_2Co_{17} structure (see Fig. 1(b). From Fig. 1(a) and (b), we can clearly see that by means of annealing treatment, the Sm_2Co_{17} nanowires changed its original amorphous phase to stable polycrystalline structure. Fig. 2(a) and (b) display the XRD patterns of Sm_2Co_{17}/Fe_7Co_3 double-phase nanowire arrays of as-deposited and annealed at 660 °C for 4 h in 99.99% Ar, respectively. As the measurement was taken with the AAO membrane, not only the diffraction peak of Al sheet (Fig. 2(a)) but also the peak of Al_2O_3 was shown (Fig. 2(b)). Moreover the XRD of the product before annealing shows no characteristic peaks of Sm_2Co_{17} (Fig. 2(a)), revealing a poor crystallinity of direct synthetic Sm_2Co_{17}, which are consistent with the as-deposited single-phase Sm_2Co_{17} (Fig. 1(a)). In addition, the strong and sharp peaks in Fig. 2(a), which can be indexed as 110 reflection from Fe_7Co_3, reveal that Fe_7Co_3 nanowires are well crystallized. For the annealed double-phase nanowires of Sm_2Co_{17}/Fe_7Co_3 however, the new diffraction peaks (Fig. 2(b)) of 122, 015, 205, and 600 appear in comparison with the single-phase nanowires (see Fig. 1(b), showing a more random distribution of hexagonal Sm_2Co_{17} grain orientations. No other impurity peaks are detected, indicating the pure Sm_2Co_{17}/Fe_7Co_3 phases.

The morphology and the attached EDS spectra of the resulting single-phase and double-phase nanowires were investigated in detail by using scanning electron microscopy (SEM) in Fig. 3. The low magnification SEM image (Fig. 3(a)) shows the wire like structure uniformly with lengths up to 40 μm. The micrograph inserted in Fig. 3(a) is the selected area enlarged magnification image of Fig. 3(a), from which it is seen that the Sm_2Co_{17} nanowires have a highly ordered structure and good orientation. When the alumina is partly dissolved (Fig. 3(b)), the Sm_2Co_{17} nanowires lean towards each other, and have uniform diameter of around 50 nm. Then, the aspect ratio is up to 800. Fig. 3(c) shows a plan-view SEM image of Sm_2Co_{17}/Fe_7Co_3 double-phase nanowire arrays. Clearly, almost all the pores of AAO templates are filled up and the quantity of the nanowires is very huge. Fig. 3(d) reveals that the Sm_2Co_{17}/Fe_7Co_3 nanowires are not only parallel to each other but also perpendicular to the surface of the AAO templates. Fig. 3(e) illustrates the elemental composition of Sm_2Co_{17}/Fe_7Co_3 nanowires measured by EDS. The presence of samarium (Sm), cobalt (Co) and iron (Fe) elements are confirmed by EDS. The EDS pattern also shows the peaks of element Al (44.79 at%) and O (28.93 at%), suggesting that these AAO templates are composed

Table 1
The composition of the plating bath.

Phase	Reagent	Concentration (m/l)
Sm_2Co_{17} amorphous	$SmCl_3$ (samarium chloride)	0.2
	$CoCl_2$ (cobalt chloride)	0.1
	H_3BO_3 (boric acid)	0.7
	$C_6H_8O_6$ (ascorbic acid)	0.05
	$NH_2 \cdot CH_2 \cdot COOH$ (glycine)	0.2
	HCl (Hydrochloride)	1.0
Fe_7Co_3	$FeCl_2$(ferrum chloride)	0.35
	$CoCl_2$ (cobalt chloride)	0.15
	H_3BO_3 (boric acid)	0.7
	$C_6H_8O_6$ (ascorbic acid)	0.05

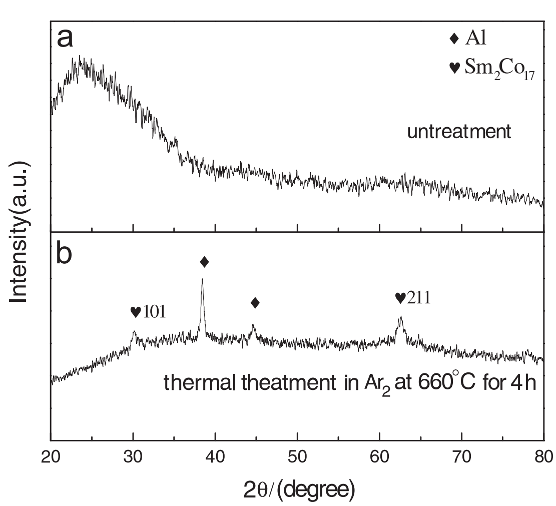

Fig. 1. X-ray diffraction patterns of Sm_2Co_{17} nanowire arrays as-deposited (a) and after thermal treatment (b) in 99.99% Ar at 660 °C for 4 h.

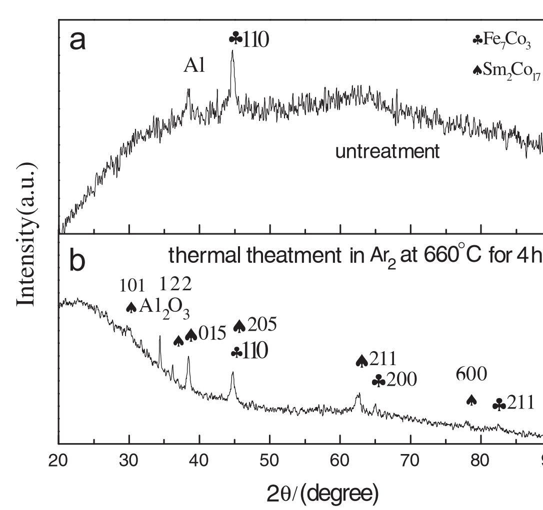

Fig. 2. X-ray diffraction patterns of Sm_2Co_{17}/Fe_7Co_3 nanowire arrays as-deposited (a) and after thermal treatment (b) in 99.99% Ar at 660 °C for 4 h.

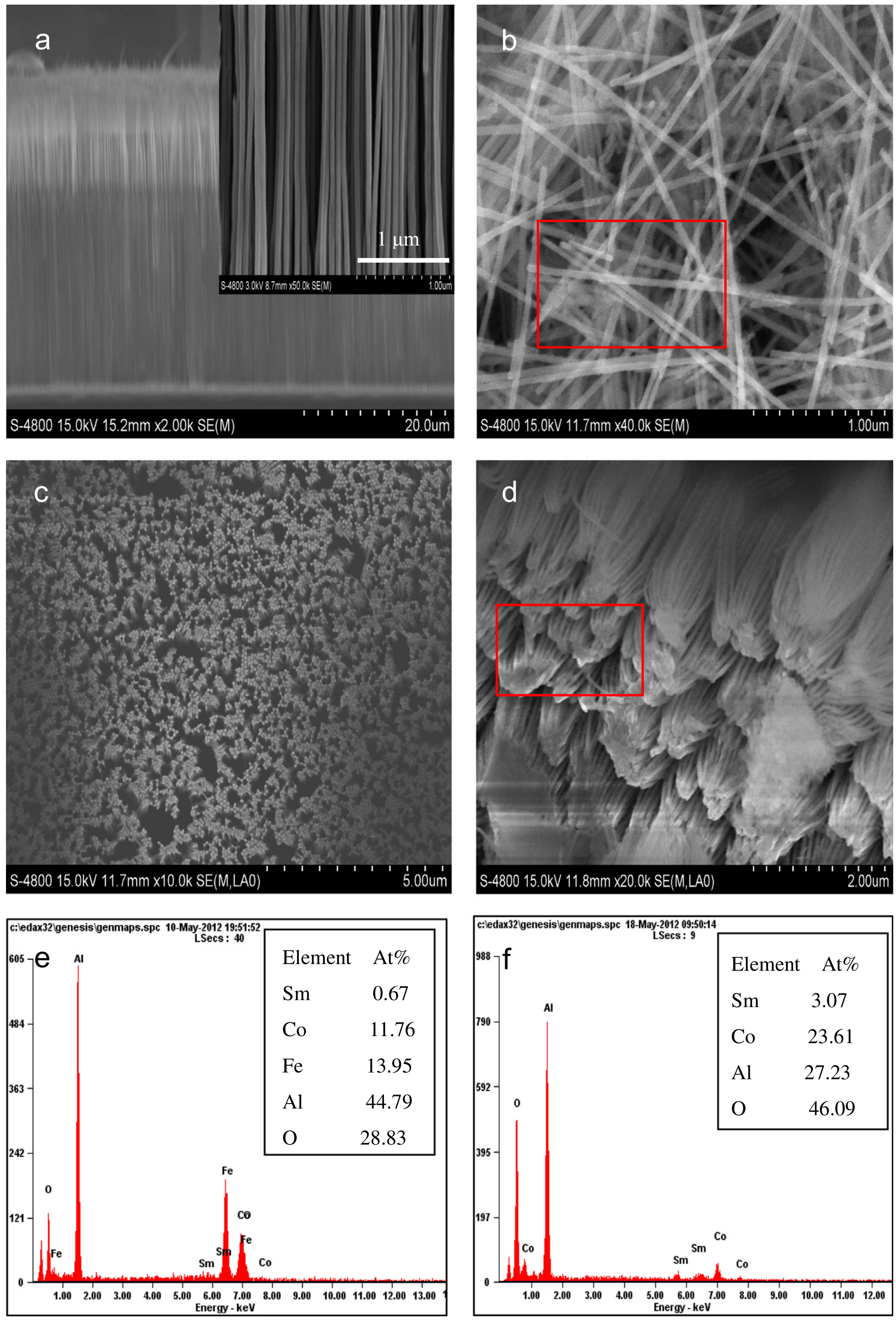

Fig. 3. SEM images and the attached EDS spectra of Sm_2Co_{17} and Sm_2Co_{17}/Fe_7Co_3 nanowires. (a) Low magnification SEM image of Sm_2Co_{17} nanowires arrays with corresponding close-up pattern in inset. (b) High-magnification of Sm_2Co_{17} nanowires after isolation from the AAO template. (c) A large scale area image of Sm_2Co_{17}/Fe_7Co_3 nanowires with AAO template partially dissolved: (d) High-magnification surface and cross-section view of Sm_2Co_{17}/Fe_7Co_3 nanowires. (e) The corresponding attached EDS spectrum of the as-synthesized nanowires as the frame in (b). (f) The corresponding attached EDS spectrum of the as-synthesized nanowires as the frame in (d).

of Al_2O_3 with the atom ratio of Al/O close to 2:3. And it should be noted that no other impurities of the elements were present in the nanowires. The inset of Fig. 3(e) shows the elemental atomic percentages of the nanowires. The atomic percentages of samarium (Sm), cobalt (Co) and iron (Fe) of the nanowires are found to be 0.67%, 11.76% and 13.95% respectively. Based on the EDS data, the molar ratio of Sm_2Co_{17} to Fe_7Co_3 can be calculated, the ratio is 1:5.88. EDS spectra in Fig. 3(f) show only Sm and Co peaks (the Al and O signals are still from the AAO template), suggesting that the single-phase nanowires are composed of Sm and Co with the atom ratio of Sm/Co close to 2:17, and thus taking into account of the uncertainty of the EDS measurement, the chemical formula of this alloy is Sm_2Co_{17}, which corresponds with the result of Fig. 1(b).

The single-phase and double-phase structures were further confirmed by TEM and selected area electron diffraction (SAED). The details of the microstructural evolution of Sm_2Co_{17} and Sm_2Co_{17}/Fe_7Co_3 nanowires are shown in Fig. 4. The single nanowires (Fig. 4(a), (d), (g)) prepared by AAO templates synthesis are

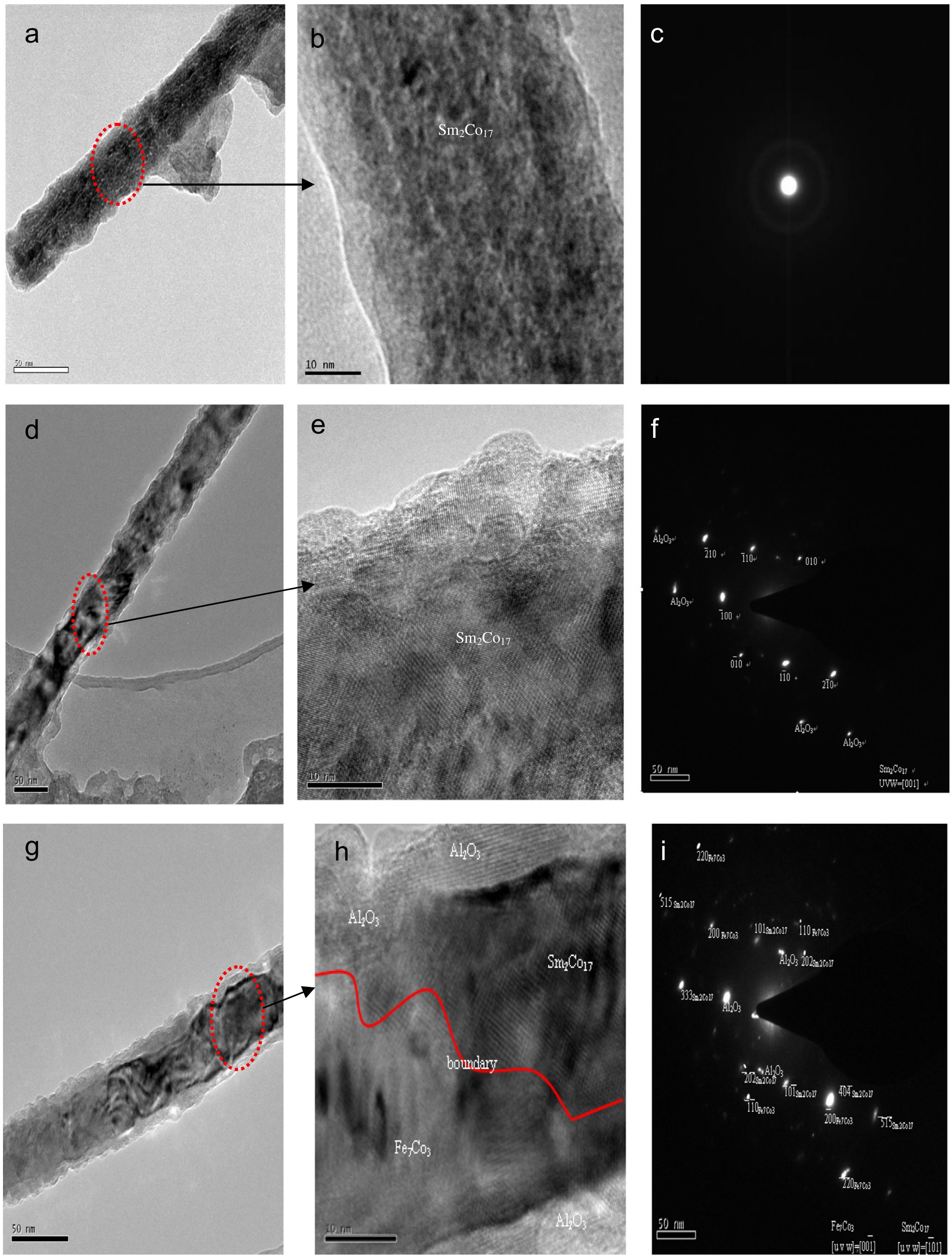

Fig. 4. TEM micrographs and SAED patterns of Sm_2Co_{17} and Sm_2Co_{17}/Fe_7Co_3 nanowires: (a) bright field image of amorphous Sm_2Co_{17}; (b) SAED of (a); (d) bright field image of annealed Sm_2Co_{17}, (e) SAED of (d); (g) bright field image of annealed Sm_2Co_{17}/Fe_7Co_3, (h) SAED of (g). And (c), (f), and (i) are HRTEM images of the nanowire shown in (a), (d), and (g).

regular size and continuous. All of them have uniform diameter of about 50 nm, which approximately equals to that of pores of the employed AAO templates.

It is clearly seen that the Sm_2Co_{17} nanowire prepared by DC electrodeposition with a constant voltage is composed of amorphous phase, evidenced by the non-lattice fringe areas formed in the nanowires as shown in Fig. 4(b). At the same time, the amorphous structure can be further confirmed by the corresponding SAED pattern (see Fig. 4(c)), which is confirmed by the XRD spectrum as shown in Fig. 1(a). Compared with the as-deposited Sm_2Co_{17} nanowires, the annealed Sm_2Co_{17} nanowires demonstrate a nearly nano-polycrystal structure as shown in Fig. 4(e), which displays the lattice fringe areas of finer crystallites with different orientations, indicating that the single annealed Sm_2Co_{17} nanowire is an agglomerate of many finer crystallites. The sizes of these finer crystallites range from 5 to 10 nm. Furthermore, the SAED pattern (Fig. 4(f) observed using a TEM micrograph, in Fig. 4 (f) encircled area, presents several sharp diffraction spots, which are observed along crystal band axis of [001] Sm_2Co_{17}. Fig. 4(h) is an HRTEM image of Sm_2Co_{17}/Fe_7Co_3 interface in Sm_2Co_{17}–Fe_7Co_3 composite with the state of annealing at 660 °C for 4 h. It is indicated that Sm_2Co_{17}/Fe_7Co_3 interface is smooth, and no intermediate phase is found in the interface. The reason is that consumption of cobalt element in the solid alloy is complete during the in situ reaction in this processing condition. Moreover, some broken ring patterns were obtained and the diffraction patterns of different grains along the nanowire indicate different orientations. These results reveal that the Sm_2Co_{17}/Fe_7Co_3 nanowires are polycrystalline, which is in accordance with the results of XRD (see Fig. 2(b)).

The magnetic properties of Sm_2Co_{17} and Sm_2Co_{17}/Fe_7Co_3 nanowires embedded in an AAO template are closely related to their microstructure and therefore to the condition of growth. The hysteresis loop of the single and double phase nanowires array measured at room temperature is shown in Fig. 5 and their magnetic parameters measured are shown in Table 2. The $H(\parallel)$ and $H(\perp)$ represented external magnetic field parallel and perpendicular to nanowires, respectively. While the as-deposited Sm_2Co_{17} nanowires were not yet annealed, the linear shapes were detected as shown in Fig. 5(a) indicating that the amorphous Sm_2Co_{17} nanowires do not show hard magnetic characteristics.

It is well known that Fe_7Co_3 is a very excellent type of soft magnetic phase, and Fe_7Co_3 nanowires possess small coercive field *Hc* but with large saturation magnetization *Ms* [10], in contrast, the annealed Sm_2Co_{17} nanowires exhibit very small squareness but with high coercive field *Hc* (see Fig. 5(b) and Table 2). It is expected that, in a multilayer nanowire system, the magnetization process of the Sm_2Co_{17} layer will be counteracted by the Fe_7Co_3 layer such that a larger magnetic field was required to reverse the magnetization of the Sm_2Co_{17} layer.

Fig. 5(c) illustrates the hysteresis loop of the as-deposited Sm_2Co_{17}/Fe_7Co_3 sample. The hysteresis curves of the nanocomposite can be described by a single-shaped loop (no staircase curve) similar to that of a single phase indicating that magnetization of

Table 2
Coercivity and squareness of Sm_2Co_{17}, Fe_7Co_3 and Sm_2Co_{17}/Fe_7Co_3 nanowires.

Sample	*Hc* (Oe) (‖)	*Hc* (Oe) (⊥)	*Mr/Ms* (‖)	*Mr/Ms* (⊥)
As-deposited Sm_2Co_{17}	469	90	0.16	0.07
Annealed Sm_2Co_{17}	817	316	0.39	0.13
As-deposited Sm_2Co_{17}/Fe_7Co_3	1042	86	0.46	0.09
Annealed Sm_2Co_{17}/Fe_7Co_3	2239	112	0.92	0.11

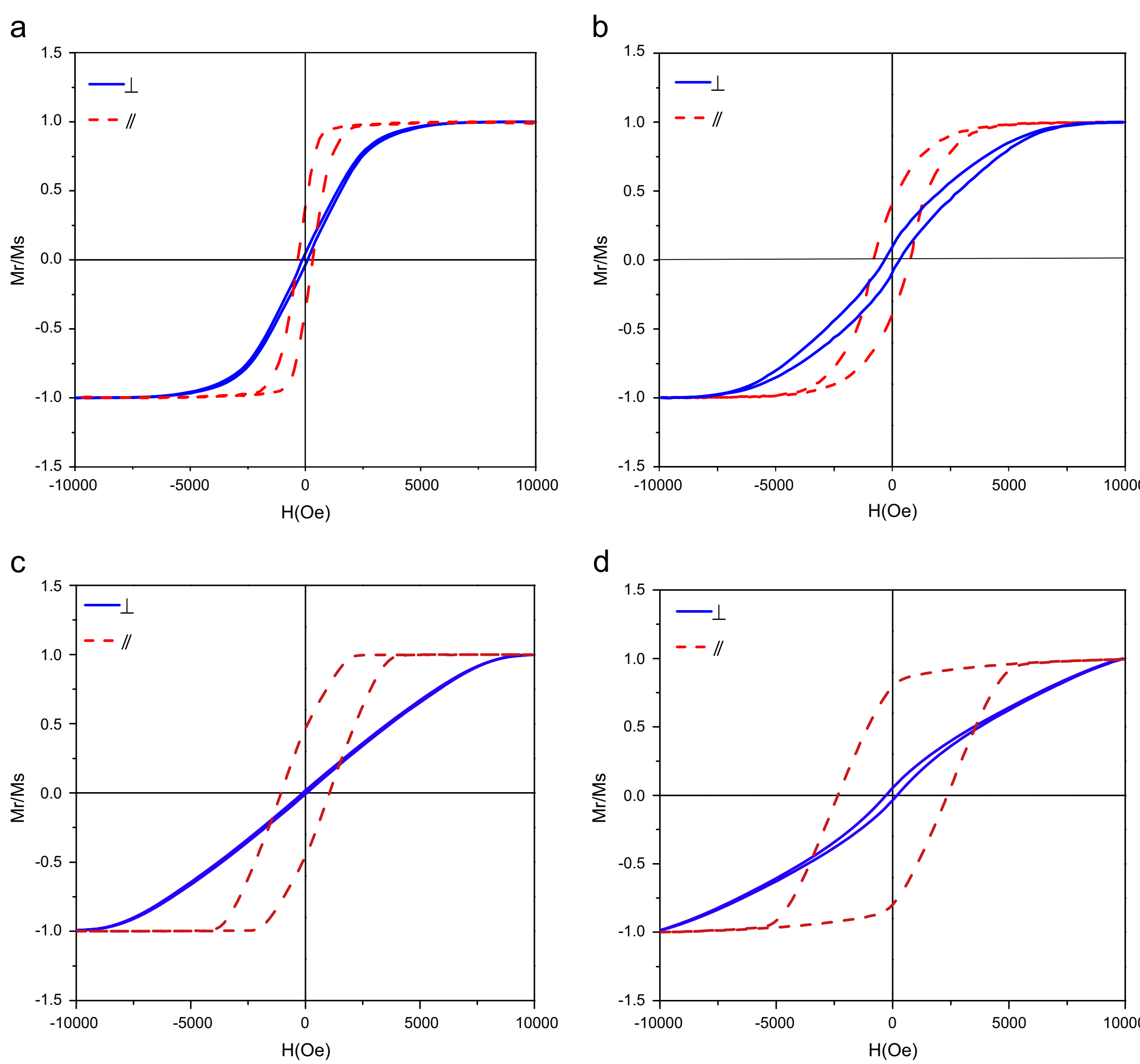

Fig. 5. Magnetization curves of Sm_2Co_{17}, Fe_7Co_3 and Sm_2Co_{17}/Fe_7Co_3 nanowires embedded in the AAO template: (a) the as-deposited Sm_2Co_{17} nanowires; (b) Sm_2Co_{17} nanowires (annealed at 660 °C for 4 h in argon atmosphere); (c) the as-deposited Sm_2Co_{17}/Fe_7Co_3 nanowires and (d) Sm_2Co_{17}/Fe_7Co_3 nanowires (annealed at 660 °C for 4 h in argon atmosphere).

both phases reverses cooperatively. A coercivity of 1042 Oe ($H(\|)$) and a squareness of 0.46 ($H(\|)$) were obtained for Sm_2Co_{17}/Fe_7Co_3 nanowires at room temperature. Because amorphous Sm_2Co_{17} nanowires and Fe_7Co_3 nanowires all display soft magnetic characteristics, then the exchange-coupling interactions between the soft–soft phase grains are enhanced, the coercive and squareness values are not greatly improved. When the double-phase nanowires are annealed at 660 °C for 4 h, both coercivity and squareness in the parallel direction are greatly improved (see Fig. 5(d)). The ratio of the remnant magnetization *Mr* to the saturation magnetization *Ms* (squareness) is about 0.92, which significantly exceeds the theoretical limit ($Mr/Ms \leq 0.5$) for the isotropic materials [11]. This suggests that Sm_2Co_{17}/Fe_7Co_3 nanowires occur inter-phase exchange coupling between the magnetic hard phase (the multicrystal Sm_2Co_{17} phase) and the magnetic soft phase (the multicrystal Fe_7Co_3 phase), which leads to magnets with improved energy products. Clearly, it was also found that the annealed nanowires exhibit a typical perpendicular magnetic anisotropy, in which the magnetic loop respectively displays the rectangular shape with the external field perpendicular to the nanowires and the linear shape with the external field parallel to the nanowires. Such a perpendicular magnetic anisotropy is dominantly attributed to the shape anisotropy of the Sm_2Co_{17}/Fe_7Co_3 nanowire.

4. Conclusion

In summary, we investigated the microstructure and magnetic properties of the Sm_2Co_{17} single-phase and Sm_2Co_{17}/Fe_7Co_3 double-phase nanowires via a DC electrodeposition with constant voltage on the anodic aluminum oxide (AAO) templates. Our XRD and HRTEM results demonstrate that the Sm_2Co_{17} nanowires deposited under a DC constant voltage has the amorphous microstructure. Subsequently, the hysteresis loop of the as-deposited and annealing double-phase arrays demonstrates inter-phase exchange coupling with soft–soft and soft–hard types, respectively.

Finally, these results can provide guidelines for the production of nanostructures with technological purposes such as the fabrication of magnetic recording devices.

Acknowledgments

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