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Structural and magnetic properties of Co and $Co_{71}Ni_{29}$ nanowire arrays prepared by template electrodeposition

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Abstract A comparative study on the structural and magnetic properties of Co and $Co_{71}Ni_{29}$ nanowire arrays prepared by AC electrodeposition in alumina templates has been presented. The Co and $Co_{71}Ni_{29}$ nanowires observed by SEM and TEM have a 45 nm diameter and exhibit high aspect ratio. Also, the nanowires of both Co and $Co_{71}Ni_{29}$, determined by XRD, have an identical crystallographic structure. The $Co_{71}Ni_{29}$ nanowires exist in a cobalt solid solution. Both the as-obtained Co and $Co_{71}Ni_{29}$ nanowire arrays measured by VSM show obvious magnetic anisotropy, dominated by shape anisotropy. Compared to the Co nanowire arrays, $Co_{71}Ni_{29}$ nanowire array shows an enhanced coercivity Hc (⊥) and approximate square ratio Mr/Ms(⊥).

Introduction

In recent years, the fabrication of magnetic nanowire arrays has become the subject of intensive study [1–3] due to their potential applications in ultra-high-density magnetic storage devices and microsensors [4]. Magnetic nanowire arrays as an ultra-high-density magnetic storage material can achieve recoding densities of more than 100 Gbit/inch^2, which is beyond the projected thermal limits of 40 Gbit/inch^2 in continuous magnetic film. A suitable template is generally needed for fabricating such magnetic arrays. Among many materials for the template, porous alumina film is one of the most ideal candidates for the template because of its self-organised, cylindrical and uniform nanoholes, of which the size can be controlled by altering the anodizing conditions and subsequent procedure. Using the alumina film as a template, an effective and simple route to fabricate the array is to deposit suitable magnetic materials in the nanoholes by an electrochemical method. To date, the arrays of ferromagnetic simple substances, such as Fe, Co and Ni, have been synthesized by the electrodeposition technique. The present works are focused on the fabrication and investigation of their alloy arrays, and a series of alloy arrays, such as FeNi [5], FeCo [6] and CoPt [7, 8] etc, have been synthesized.

Co–Ni alloy has many advantages such as mechanical properties [9, 10] and electrocatalytic activity [11], especially its magnetic properties, which make it be extensively applied in many industrial fields. At the same time, Co^{2+} and Ni^{2+} ions have an almost similar value of standard electrode potentials, so the Co^{2+} and Ni^{2+} ions can be easily performed co-deposition in a common acidic solution, which especially essential for a template electrodeposition process due to the fine nanoscale holes in the alumina film.

In this work, $Co_{71}Ni_{29}$ nanowire array, using the alumina template, has successfully been fabricated by AC electrodeposition. A comparative study on the structural and magnetic properties of $Co_{71}Ni_{29}$ and pure cobalt nanowire arrays has been carried out by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersed X-ray spectrometry (EDS), X-ray diffraction (XRD) and vibrating sample magnetometer (VEM).

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Experiment

A two-step anodic oxidation method had been applied to prepare the alumina template. The details had been reported in our past work [12]. After anodization, a technique of reducing the anodization volatage to 10 V in a series of small steps, as described in Ref. [13], was applied to thin the barrier layer in order to increase the deposition rate during the AC electrodeposition. The electrolytes of Co and $Co_{71}Ni_{29}$ nanowires contained $CoSO_4{\cdot}7H_2O$ 40 g/L; H_3BO_3 25 g/L and $CoSO_4{\cdot}7H_2O$ 40 g/L; $NiSO_4{\cdot}7H_2O$ 110 g/L, H_3BO_3 25 g/L, respectively. Also, a little of saccharine had been added in the electrolytes to better the AC electrodeposition. All the reagents used were AR purity. The pH values of electrolytes were maintained at 3.0–4.0. Both Co and $Co_{71}Ni_{29}$ nanowire arrays had been deposited with graphite as counter electrode and the porous alumina template with aluminum plate as working electrode at room temperature. The voltages and the frequencies of sine wave used in AC electrodepositions were 20.0 V and 200 Hz, respectively.

The morphologies of the as-obtained nanowire arrays were observed by scanning electron microscopy (SEM:JEOL JSM-5600 operating at 15 kV). Transmission electron microscopy (TEM:FEI TECNAI20 working at 200 kV) was employed to survey the cobalt and $Co_{71}Ni_{29}$ nanowires liberating from the alumina film. The crystalline structures of the cobalt and $Co_{71}Ni_{29}$ nanowires were investigated by X-ray diffraction (XRD: D/Max-RB diffractometer with Cu Kα radiation). The magnetic properties of Co and $Co_{71}Ni_{29}$ nanowire arrays were measured by VSM (VSM:Lakeshore, Model 7300 series) at room temperature. The applied magnetic field was 10 kOe.

Result and discussion

The alumina template prepared by the two-step anodic oxidization is shown in Fig. 1. From the images, a highly ordered alumina template with identical about 45 nm diameter and about 65 nm interval of the holes has been obtained. The aspect ratio of the holes (depth to diameter) is great (more than 1,000). At the same time, the parameters above are easily regulated by altering the conditions of anodic oxidation. The typical morphology of the Co and $Co_{71}Ni_{29}$ nanowires has been indicated by the SEM image of the as-obtained array (shown in Fig. 2). The nanowires have an identical diameter. Due to the loss of alumina sustainment and high surface energy of the nanowires, the nanowires tend to be gathered into bunched structure. It can too be seen that some tiny blocks of alumina templates with many nanoholes are not dissolved thoroughly and remained in the Fig. 2.

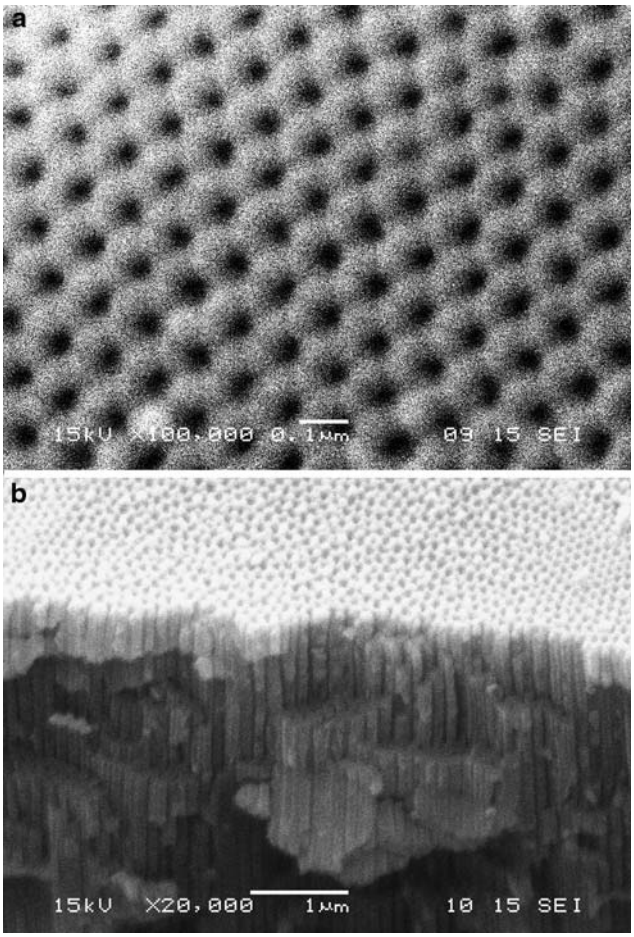

Fig. 1 SEM images of the alumina template by two-step anodic oxidization (**a**) surface, (**b**) section

The $Co_{71}Ni_{29}$ nanowires with removal of alumina template, determined by means of TEM, are shown in Fig. 3. It can be seen that the nanowire has an about 45 nm diameter corresponding to the nanoholes size of the alumina template. At the same time, the nanowire exhibits a great aspect ratio. For determining the nanowires in a quantitative way, energy dispersive spectra (EDS) associated with SEM has been applied to investigate the CoNi alloy nanowires. The result, shown in Fig. 4, indicates that the atomic ratio (Co to Ni) is 71:29. Therefore, the $Co_{71}Ni_{29}$ nanowires array has been obtained in our present work.

An identical crystallographic structures can easily been decided by XRD of cobalt and $Co_{71}Ni_{29}$ nanowires array (in Fig. 5). Except for the diffraction of aluminium, there is only a peak (002) of cobalt with

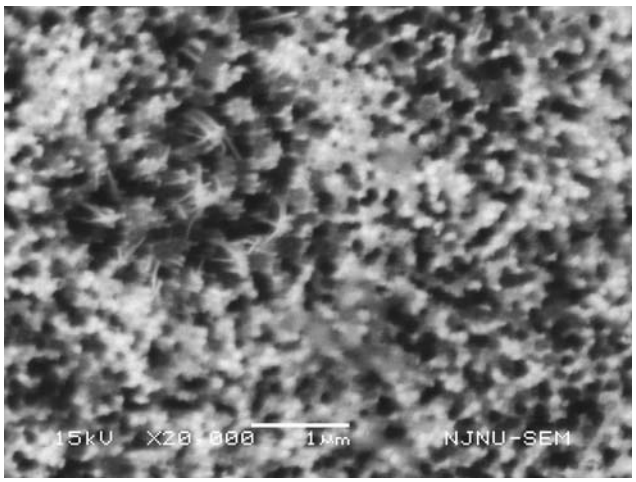

Fig. 2 Typical SEM image of the Co and $Co_{71}Ni_{29}$ nanowire arrays by dissolving partly the alumina template in a H_3PO_4 and H_4CrO_4 solution for 15 min

hcp phase for the Co and $Co_{71}Ni_{29}$ nanowires in the XRD patterns of Co and $Co_{71}Ni_{29}$ nanowires arrays. So, it is concluded that $Co_{71}Ni_{29}$ nanowires existed in a Co solid solution with hcp phase and an obvious preferential orientation [002]. According to the phase diagram of binary Co–Ni system, a mixed structure of fcc and hcp phase should be formed in $Co_{71}Ni_{29}$ alloy. A phase offset in contrast to $Co_{71}Ni_{29}$ equilibrium phase has been formed in the as-obtained sample. The cause is attributed to the quick deposition of $Co_{71}Ni_{29}$ nanowire during the process of ac electrodeposition.

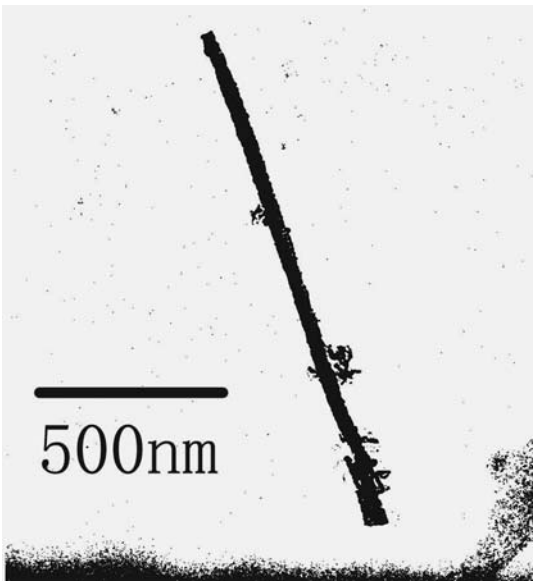

Fig. 3 TEM image of a single $Co_{71}Ni_{29}$ nanowire liberating from the alumina template

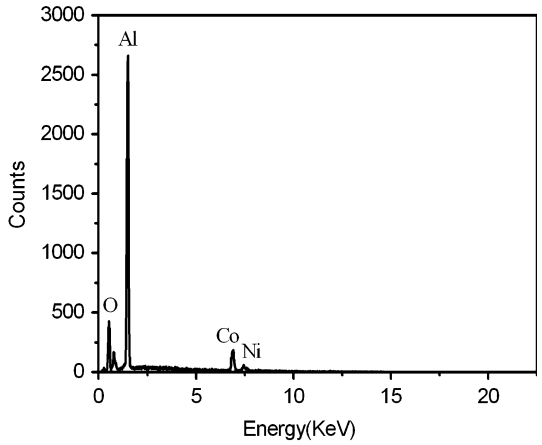

Fig. 4 EDS spectra of Co–Ni alloy nanowires, indicates that the atomic ratio (Co:Ni) is 71:29

The hysteresis loops of both cobalt and $Co_{71}Ni_{29}$ nanowire arrays determined by VSM are shown in Fig. 6. Obvious magnetic anisotropies have been indicated from the hysteresis loops. The directions perpendicular to the alumina templates, i.e., along with the axis of the nanowire, are easy to magnetize and the hard directions are parallel to the templates, i.e., vertical to the axis of the nanowire, for both cobalt and $Co_{71}Ni_{29}$ nanowire arrays. Furthermore, the values of coercivity Hc (⊥) and square ratio Mr/Ms(⊥) for $Co_{71}Ni_{29}$ nanowire array are 2.073 kOe and 0.791, respectively. However, they were 1.641 kOe and 0.758 for the pure Co nanowire array. Compared to the Co nanowire arrays, $Co_{71}Ni_{29}$ nanowire array shows an enhanced coercivity Hc (⊥) and approximate square ratio Mr/Ms(⊥). It is well-known that the magnetic anisotropy is from magnetocrystalline anisotropy and

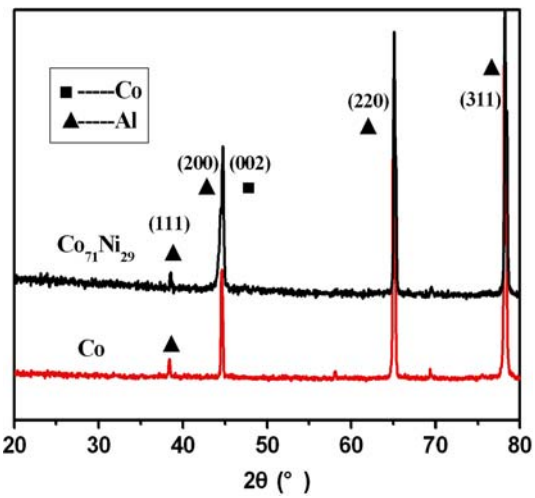

Fig. 5 XRD patterns of cobalt and $Co_{71}Ni_{29}$ nanowire arrays

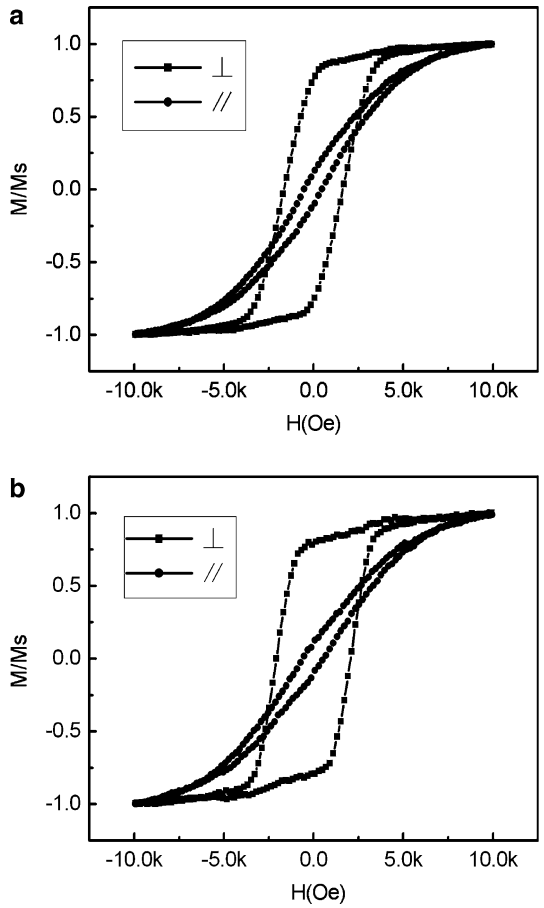

Fig. 6 Hysteresis hoops with the magnetic field applied parallel (●) and perpendicular (■) to the surface of Co (**a**) and $Co_{71}Ni_{29}$ (**b**) nanowire arrays

shape anisotropy. For the as-obtained cobalt and $Co_{71}Ni_{29}$ nanowires, a similar geometric shape with huge aspect ratio has observed by TEM. Therefore, the nanowires can be regarded as infinite circular columns, in which the demagnetizing factor along the nanowires is 2π and perpendicular to them is 0. In the absence of an external field this shape anisotropy compels the magnetization to be along the nanowires direction. A highly desirable perpendicular magnetization should be a natural consequence of the geometry of the cobalt and $Co_{71}Ni_{29}$ nanowire arrays. In conclusion, we conclude that it is the identical geometric shape and crystallographic structure that they decide the similar shape anisotropy and magnetocrystalline anisotropy, i.e., similar magnetic anisotropy for the cobalt and $Co_{71}Ni_{29}$ nanowire arrays. Consequently, the arrays of cobalt and $Co_{71}Ni_{29}$ nanowires have an approximate value of square ratio Mr/Ms(⊥). The enhanced coercivity Hc (⊥) of $Co_{71}Ni_{29}$ nanowire array may be attributed to the high defects of $Co_{71}Ni_{29}$ nanowires, caused by nickel doped in the cobalt nanowires.

Conclusion

Using the highly-ordered alumina template, the arrays of Co and $Co_{71}Ni_{29}$ nanowires have been fabricated by AC electrodeposition technique. The as-obtained nanowires have an identical 45 nm diameter and exhibit huge aspect ratio. XRD patterns indicate that there is an identical crystallographic structure. The $Co_{71}Ni_{29}$ nanowires exist in a Co solid solution, and an hcp single-phase structure with an obvious [002] texture. The magnetic properties of both the cobalt and $Co_{71}Ni_{29}$ nanowire arrays measured by VSM show obvious magnetic anisotropy, which the direction perpendicular to the alumina template is easy to magnetize and the hard direction is parallel to the templates. Compared to the Co nanowire arrays, $Co_{71}Ni_{29}$ nanowire array shows an enhanced coercivity Hc (⊥) and appropriate square ratio Mr/Ms(⊥). It is the similar geometric shape and crystallographic structure of Co and $Co_{71}Ni_{29}$ nanowires that they decide the approximate square ratio Mr/Ms(⊥).The increased coercivity Hc(⊥) may be attributed to the defects of $Co_{71}Ni_{29}$ nanowires, caused by nickel doped in the cobalt nanowires.

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