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AC electrodeposition frequency dependence of composition and magnetic properties of Fe-Co nanowire arrays

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Abstract: Fe-Co alloy nanowire arrays with the interwire distance of about 50 nm and the wire diameter of about 22 nm were fabricated by alternating current electrodeposition at different frequencies into anodic aluminum oxide templates. The influences of the deposition frequency on the composition, crystalline structure and magnetic properties of the arrays were studied in detail. It was found that the deposition frequency for the Fe-Co alloy nanowire arrays has an optimal range of 5～350 Hz. For the arrays prepared within this range, the deposition frequency has no obvious influence on their crystalline structure, while it does affect the array's composition and magnetic properties. The variations for the nanowire's saturation magnetization and the magnetostatic interaction between nanowires were employed to explain the change in the array's magnetic properties with the deposition frequency qualitatively. After annealing in hydrogen atmosphere, all the arrays fabricated within the optimal frequency range have fairly good magnetic properties. Their coercivities and squarenesses are higher than 3.512 kOe and 0.939, respectively. The array deposited at 50 Hz possesses the comparatively best hard magnetic performance. The thermomagnetic analysis indicates that its Curie temperature is about 630 ℃.

Key words: Fe-Co nanowire array; AC electrodeposition; frequency; composition; magnetic properties

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交流电沉积频率对 Fe-Co 纳米线阵列的成分和磁性能的影响

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摘要:采用交流电沉积方法于不同频率在氧化铝模板中合成了线间距 50 nm、直径 22 nm 的 Fe-Co 合金纳米

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线阵列,研究了沉积频率对阵列成分、晶体结构以及磁性能的影响.研究发现:Fe-Co 纳米线阵列的最佳沉积频率范围为 5～350 Hz.在此范围内合成的阵列,其晶体结构对沉积频率的依赖并不明显,但成分与磁性能却会受到沉积频率的影响.阵列磁性能随频率的变化趋势可以用纳米线饱和磁化强度与线间静磁耦合作用的改变来定性解释.氢气退火后,所有阵列均具有良好的磁性能.它们的矫顽力和矩形度分别高于 3.512 kOe 和 0.939.其中,50 Hz 沉积的阵列磁性能相对最好.热磁分析表明:其居里温度约为 630 ℃.

关键词:Fe-Co 纳米线阵列;交流电沉积;频率;成分;磁性能

0 Introduction

Magnetic nanowire arrays have been studied widely for more than two decades owing to their applications in fundamental scientific studies of nanomagnetics and advanced nanotechnologies, such as magnetic storage, magnetotransport, magnetic device, etc.[1~3]. Among numerous kinds of magnetic nanowire arrays, Fe-Co array has attracted much attention in recent years due to the following properties of Fe-Co alloy: good antioxidant ability, low-temperature coefficients of the coercivity and the remanence, high Curie temperature, and the highest saturation magnetization in transition metals and alloys[4~15]. Hereinto, Zhan et al.[4] investigated the crystalline structure and the magnetic properties of Fe-Co nanowires with different compositions and found that nanowires with various compositions possess different structures (bcc, fcc, hcp) and the magnetization reversal model based on "chains of spheres" and the symmetric fanning mechanism can be used to explain the composition dependence of the magnetic properties; Pierce et al.[5] fabricated the Fe-Co alloy nanowires along the atomic step edges of a miscut W (110) surface; Qin et al.[6,7] studied the influences of the annealing temperature and the composition on the Fe-Co nanowire arrays' crystalline structure and magnetic properties and found that the variation of the nanowire's microstructure, saturation magnetization and magnetic anisotropy can be used to interpret the dependence of the magnetic properties on the composition and the annealing temperature; Lee et al.[8] prepared Fe-Co nanowires by thermally decomposing the $Fe(CO)_5/Co_2(CO)_8$ metal carbonyl vapors; Fordor et al.[9] studied the crystalline structure and the magnetic properties of Fe-Co nanowires with different compositions and found that magnetostatic interaction between the nanowires has a significant effect on the array's magnetic properties; Jo et al.[14] investigated the electronic structures and magnetic properties of Fe-Co nanowires by the density functional theory calculations using the ultrasoft pseudopotential plane wave method and found that the chain-of-spheres model can be used to estimate the nanowire array's coercivity. In the past four years, we also investigated the properties of Fe-Co nanowire arrays with different geometry sizes and different compositions in detail[10~13,15]. It was found that the magnetostatic interaction between nanowires influences the array's magnetic properties obviously. Through regulating the interwire distance D_i and the wire diameter D_w, the highest reported coercivity (H_c = 3.99 kOe) and squareness (M_r/M_s = 0.96) for nanowire arrays were obtained in $Fe_{48}Co_{52}$ nanowire array with D_i of about 50 nm and D_w of about 22 nm.

As one of the simplest and the most inexpensive methods, electrodeposition into the anodic alumina template, instead of e-beam lithography and chemical vapor deposition, is usually employed to prepare the nanowire arrays. Generally, it consists of two types, the alternating current (AC) electrodeposition and the direct current (DC) electrodeposition. The former is simpler and amenable to industrial scale processing, because it requires fewer processing steps, such as removing the aluminum substrate and the alumina barrier layer[16]. For the AC method, the deposition parameters, including pH

value, voltage, deposition time, etc., have been proved to have great influences on the growth and the performance of the nanowire arrays[1]. However, the literatures about the frequency dependence of the deposition of nanowire arrays are limited and the studying materials were only elementary metals, including Co, Bi, Ni, Au, etc.[16~18]. According to these studies, the frequency has a great effect on the deposition of nanowire array and the optimal deposition frequency range varies with the deposited material.

Until now, the dependences of the composition and the magnetic performance on the AC electrochemical deposition frequency for Fe-Co alloy nanowire array have not been reported yet. Therefore, we selected Fe-Co arrays with D_i of about 50 nm and D_w of about 22 nm as the studying objects in this work due to their good hard magnetic performance[12,13] and reported for the first time their optimal deposition frequency range and the influences of the deposition frequency on their composition, crystalline structure and magnetic properties.

1 Experimental

Highly ordered porous alumina templates were prepared by anodic oxidation of 99.999% pure Al foil with a nominal thickness of 300 μm in sulphuric acid solution via a two-step electrochemical anodization process. To obtain templates with D_i of about 50 nm, anodization was firstly carried out at the voltage of 20 V in 0.3 mol/L H_2SO_4 at 0 ℃ for 12 h. The formed alumina was then removed by a mixture of 0.4 mol/L H_3PO_4 and 0.2 mol/L H_2CrO_4 at 60 ℃ for 15 h, and the Al sheet was reanodized under the same conditions as the first step for 8 h. To get the pore diameter of about 22 nm, the templates were etched in 0.3 mol/L H_3PO_4 at 30 ℃ for 1 min.

The Fe-Co nanowires were electrodeposited in an electrolyte consisting of 0.095 mol/L $FeSO_4 \cdot 7H_2O$, 0.125 mol/L $CoSO_4 \cdot 7H_2O$, 0.6 mol/L boric acid, and 1 g/L ascorbic acid at room temperature under AC conditions. The pH value of the electrolyte was kept at about 4.0. The deposition voltage and time were 16 V and 15 min, respectively. The AC wave adopted in electrodeposition was sine form. The deposition frequency ranged from 2 to 500 Hz. To obtain good magnetic properties, the as-deposited arrays were annealed at 550 ℃ in hydrogen atmosphere for 24 min.

Scanning electron microscopy (SEM, Hitachi, S-3400N II) and transmission electron microscopy (TEM, JEOL JEM-100S) were applied to characterize the morphologies of the alumina templates and nanowires, respectively. X-ray diffraction (XRD, D/Max-RA with Cu K_α radiation) and induction-coupled plasma spectrometer (ICP, Jarell-Ash, J-A1100) were used to investigate the crystalline structure and the composition of nanowire arrays, respectively. Magnetic properties were measured by a vibrating sample magnetometer (VSM, Lakeshore, Model 7 300 series).

2 Results and discussion

During the experimental process, it was found that there exists an optimal frequency range for depositing the Fe-Co alloy nanowires. High quality deposition can only be obtained with AC frequency ranging from 5 to 350 Hz. If the frequency is beyond this range, there is very little or even no deposition. In the case where the frequency is lower than 5 Hz, it can be attributed to the large deposition period per cycle which makes the deposition almost the same as DC deposition[18]. Therefore, the existence of the alumina barrier layer results in a low deposition current and a slow deposition rate. When the deposition frequency is higher than 350 Hz, the situation is different. It may be due to the high charging current of solution double layer capacitor under high frequency leading to an extremely slow deposition rate[17].

For the arrays deposited within the optimal frequency range, their morphology, composition,

crystalline structure and magnetic properties were investigated in detail. Fig. 1(a) shows the typical TEM image of the annealed Fe-Co nanowires deposited at 50 Hz. It is obvious that the nanowires are regular and uniform with an average diameter D_w of about 22 nm. The inset of Fig. 1(a) is the electron diffraction pattern of the nanowires. The diffraction rings, which reveal that the nanowires are polycrystalline, can be identified as reflections from the body-centered-cubic (bcc) Fe-Co alloy. This can be further confirmed by the following XRD patterns. Fig. 1(b) shows the SEM image of the porous anodic aluminum oxide (AAO) template. It can be seen that the pores whose average diameter conforms to that of the nanowires are highly ordered. Their average interpore distance, namely the interwire distance D_i, is about 50 nm.

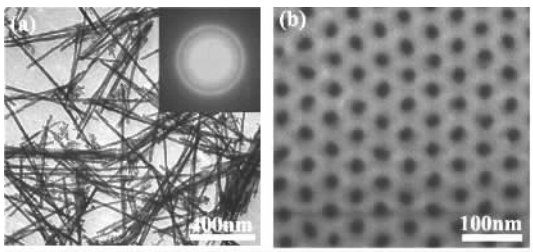


Fig. 1 TEM image and electron diffraction pattern (inset) of annealed Fe-Co nanowires deposited at 50 Hz (a) and SEM image of a representative porous alumina template (b)

ICP was used to investigate the composition of the nanowire arrays. It was found that the compositions of the arrays almost have no change after annealing. Therefore, we only show the compositions of the annealed arrays here and discuss their dependences on the deposition frequency. Fig. 2 shows the compositions of the annealed arrays deposited at the frequency ranging from 5 to 350 Hz. It can be seen that the array's composition varies with the deposition frequency. With the increase of the frequency, the Fe content x of the array fluctuates within the range of 45 at. %～55 at. % and shows a decreasing tendency as a whole. This implies that the variation of the deposition frequency has different influences on the deposition rates of Fe and Co. Although these arrays have different compositions, their crystalline structures were found to be basically identical due to their narrow composition range[4]. Fig. 3 shows their XRD patterns. We can see that these patterns are similar to those reported previously[4,6,9～13]. All the arrays have a bcc structure and prefer [110] orientation along the axis of the wire. This indicates that the deposition frequency has no obvious influence on the crystalline structure of the Fe-Co alloy within the optimal frequency range. Besides the (110) diffraction peak of Fe-Co alloy, broad peaks extending from 10° to 40° can also be found in the XRD patterns. These are caused by the amorphous AAO template.

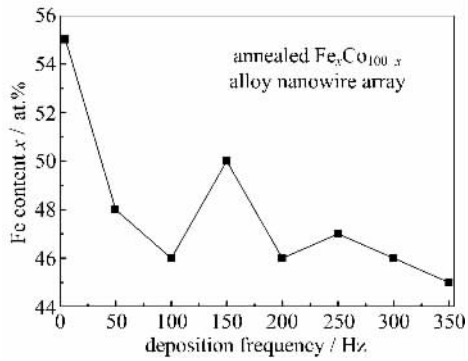


Fig. 2 Fe content x within annealed Fe_xCo_{100-x} nanowire arrays deposited at the frequency ranging from 5 to 350 Hz

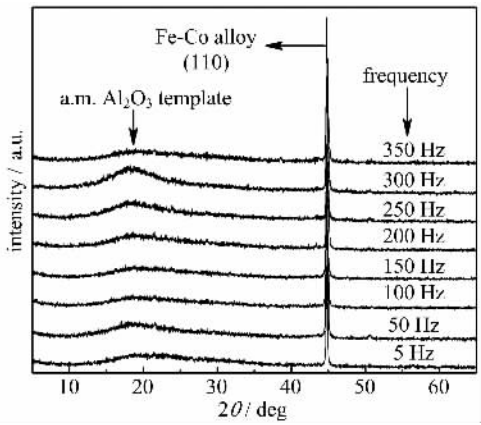
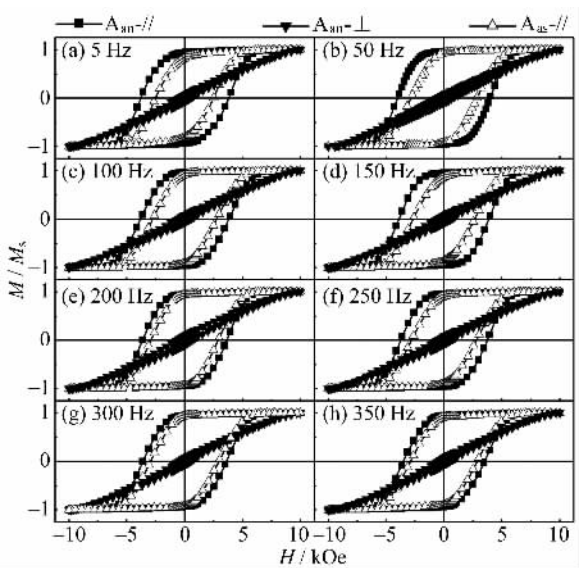


Fig. 3 XRD patterns of annealed Fe-Co nanowire arrays deposited at the frequency ranging from 5 to 350 Hz

Figs. 4(a)～(h) show the normalized room-temperature hysteresis loops of the Fe-Co nanowire arrays deposited at 5 Hz (a), 50 Hz (b), 100 Hz

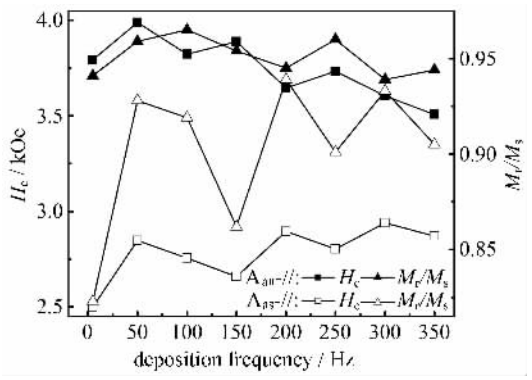
(c), 150 Hz (d), 200 Hz (e), 250 Hz (f), 300 Hz (g) and 350 Hz (h), respectively. It can be seen that the magnetic properties measured in the direction parallel to the wire axis (//) are much better than those measured in the direction perpendicular to the wire axis (⊥). Clearly, the easy axes for these arrays are along the wire and perpendicular to the template surface. This implies that the shape anisotropy for the nanowires is very strong and much higher than the magnetocrystalline anisotropy of Fe-Co alloy. Comparing the magnetic properties measured along the wire, we can also find that they are improved obviously after annealing and the annealed array deposited at 50 Hz possesses the relatively best magnetic performance. The coercivity H_c and the squareness M_r/M_s for this array are as high as 3.993 kOe and 0.959, respectively.



A_{an} and A_{as} represent the annealed array and the as-deposited one, respectively

Fig. 4　Normalized room-temperature hysteresis loops for Fe-Co nanowire arrays deposited at 5 Hz (a), 50 Hz (b), 100 Hz (c), 150 Hz (d), 200 Hz (e), 250 Hz (f), 300 Hz (g) and 350 Hz (h) with the applied field parallel (//) and perpendicular (⊥) to the wire axis

In order to show the dependence of the magnetic properties on the deposition frequency more clearly, we exhibit the coercivity H_c and the squareness M_r/M_s measured along the wire (//) as functions of the frequency in Fig. 5. It is obvious that the magnetic properties of all the arrays are improved greatly by the annealing treatment. As Qin et al.[6,7] reported previously, the annealing treatment can reduce the nanowire's internal stress and increase the nanowire's crystallinity. This is in favor of increasing the nanowire's saturation magnetization M_s. Furthermore, the large mismatch between the thermal expansion coefficients of Fe-Co alloy and the alumina template induces the Fe-Co crystallites growing along the wire axis during the annealing process. It is such increases of M_s and the crystallite size along the wire axis that result in the great improvement of the magnetic properties after annealing[6,7,10~12]. With the increase of the deposition frequency, both H_c and M_r/M_s for the annealed arrays fluctuate within a relatively narrow range (H_c = 3.512 ~ 3.993 kOe, M_r/M_s = 0.939 ~ 0.965). Observing the variation of H_c carefully, we can also find that it shows a weak decreasing tendency as a whole with the deposition frequency increasing. For these nanowire arrays with high shape anisotropy, their H_c is basically in direct proportion to the nanowire's M_s[7]. As mentioned above, the Fe content within the nanowires decreases from 55 at.% to 45 at.% with the deposition frequency increasing from 5 to 350 Hz.



A_{an} and A_{as} represent the annealed array and the as-deposited one, respectively

Fig. 5　Room-temperature coercivity H_c and squareness M_r/M_s measured along the wire (//) as functions of deposition frequency

According to the Slater-Pauling curve, such a decrease in the Fe content results in a slight increase of M_s for Fe-Co alloy. Therefore, the coercivity H_c for our arrays should present a weak increasing tendency with the increase of the deposition frequency, as Qin et al.[7] have reported. But the experimental results show a totally converse variation tendency unexpectedly, which suggests that the coercivity H_c of these arrays may not be merely determined by the nanowire's saturation magnetization M_s.

However, this seems reasonable when the magnetostatic interaction between nanowires is taken into account, which does have an influence on the array's magnetic properties[12,19,20]. Generally, such a magnetostatic interaction is determined by the array's geometry characteristics, including the wire diameter D_w, the interwire distance D_i, the pore filling ratio R_p of the template, etc., and the nanowire's saturation magnetization M_s. The decrease of D_i and the increases of D_w, R_p and M_s may increase the magnetostatic interaction undoubtedly. For the arrays discussed here, they have the same D_i and D_w. Thus, the change of the magnetostatic interaction is mainly determined by R_p and M_s. From the above discussion, we know that M_s has a slight increase with the frequency increasing. As to R_p, it also increases, as reported previously, with the increase of the AC deposition frequency[17]. Therefore, the enhanced magnetostatic interaction can be available within the array deposited at the high frequency. As discussed in many previous works, it is such an enhancement of the magnetostatic interaction that results in the decrease of H_c[11,12,19,20]. Based on these discussions, it is clear that the variation of the array's coercivity H_c with the deposition frequency is mainly determined by the changes of the nanowire's saturation magnetization M_s and the magnetostatic interaction between nanowires. With the increase of the deposition frequency, the competition of the slight increase of M_s and the enhancement of the magnetostatic interaction results in the array's H_c fluctuating within a narrow range and showing a weak decreasing tendency.

For the Fe-Co alloy nanowire array with the relatively best magnetic performance (namely the annealed array deposited at 50 Hz), its thermomagnetic property was also investigated. Its magnetization versus temperature curve measured at the field strength of 1 kOe is shown in Fig. 6. It can be seen that the magnetization keeps unchanged firstly and then decreases gradually with the temperature increasing from room temperature to 540 ℃. With further increase of temperature, the magnetization decreases sharply to zero at around 630 ℃. This very temperature is the Curie temperature (T_c) of the Fe-Co alloy nanowire array possessing the relatively best hard magnetic properties. But it is much lower than that of the bulk Fe-Co alloy (about 980 ℃). To explain this phenomenon, we should emphasize that the wire diameter for this array is only about 22 nm. According to Sun et al.[21], such a small nanowire's diameter can constrain the growth of the correlation length with increasing temperature. And it is this finite-size effect that leads to the decrease of T_c for the nanowires with a small diameter.

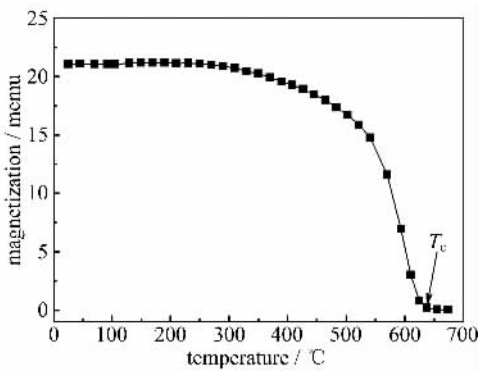


Fig. 6 Magnetization versus temperature curve for Fe-Co nanowire array deposited at 50 Hz

3 Conclusion

In conclusion, Fe-Co alloy nanowire arrays

with good hard magnetic properties were prepared within the AAO templates by AC electrochemical deposition at frequencies ranging from 5 to 350 Hz. The crystalline structure of the array showed no obvious dependence on the deposition frequency within this range, while the array's composition and magnetic properties varied with the frequency. The variation of the array's magnetic properties was explained by the competition between the change of the nanowire's saturation magnetization and that of the magnetostatic interaction between nanowires qualitatively. For all the arrays, their magnetic properties were improved greatly by annealing. The coercivities from 3.512 to 3.993 kOe and the squarenesses from 0.939 to 0.965 were obtained in the annealed arrays. The annealed array deposited at 50 Hz possessed the relatively highest magnetic performance. Its Curie temperature was found to be about 630 ℃.

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