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A study on phase relations and texture of $Co_{1-x}Pt_x$ (0.09<x<0.86) nanowire arrays

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ABSTRACT

Based on Rietveld refinement of X-ray diffraction patterns, the phase structure and microstructural parameters of $Co_{1-x}Pt_x$ nanowires are determined for a range of Pt content. The phase structure of the as-deposited $Co_{1-x}Pt_x$(0.09<x<0.86) nanowire arrays changes progressively from hcp ε-Co to a mixture of the hcp ε-Co and fcc α-Co,Pt solid solution and finally to pure fcc Co,Pt solid solution with Pt content increasing . Moreover, the texture parameter $P_{(111)}$ has a maximum value with Pt content of 50% confirmed by the (111) pole figure measurement. It is suggested that this contributes to enhance magnetocrystalline anisotropy, resulting in a relatively high squareness and coercivity for the nanowires.

1. Introduction

CoPt alloy is a potential material for high density magnetic recording media as a result of the large magnetocrystalline anisotropy associated with the ordered face-centred tetragonal (fct) phase (L_{10} structure). But the CoPt alloy prepared at various deposition conditions and heat treatments usually form the different phases, predicated by the phase diagram at room temperature, known as the metastable phase [1]. Hence the variation of the crystallographic structure in a wide range of composition is more complicated and the results of structure analyses given by authors differ somewhat [1–6]. XRD measurements [6] showed that the crystal structure of the as-deposited $Co_{1-x}Pt_x$ nanowire arrays with increasing Pt content. These results were used to explain the relationship between magnetic properties and composition-dependence of the as-deposited $Co_{1-x}Pt_x$ nanowire arrays. However, precise parameters for the microstructure (including lattice parameters, microcrystalline size and degree of grain preferred orientation) have yet to be determined.

In this work, to better understand the relation between these compositional and structural factors and the magnetic properties, Rietveld refinement method [7–9] is used to analyse the XRD patterns of the phases found in the Co–Pt alloy and to simulate XRD experimental data using full profile fitting. The (111) pole figure measurement and ODF (Orientation Distribution Function) analysis are used to explain the degree of grain preferred orientation.

2. Experimental

Arrays of $Co_{1-x}Pt_x$ (0.09<x<0.86) alloy nanowires were fabricated by electro-deposition with AAO (anodic aluminum oxide) as a template. The AAO templates used in this work were prepared by an anodization process as described previously [10]. The electrochemical deposition was carried out with a 13.6 V AC voltage (200 Hz) at room temperature. The electrolytes in this work consisted of 1 g/l H_2PtCl_6, × g/l $CoSO_4 \cdot 7H_2O$ (x = 80, 40, 20, 18, 10, 5, 1), and 30 g/l H_3BO_3. The chemical compositions of the nanowire arrays were determined by SEM equipped with EDS. The crystallographic structure and microstructural parameters of nanowires were characterized by XRD using Cu K_α radiation in the range 30–80° with a step width of 0.02°. Magnetic measurements were carried out by VSM (vibrating sample magnetometer). The XRD patterns of ε-Co, α-Co,Pt, disordered fcc CoPt phase and super lattice CoPt were calculated by Rietveld analysis with X'Pert plus software (Philips) and the ICSD data base[11] for order CoPt (AuCuI type structure) and order $CoPt_3$ ($AuCu_3I$ type structure). The (111) pole figure measurement was performed by D_{max} X-ray diffractometry (Rigaku) with Cu K_α radiation 40 kV, 40 mA, title angle of θ = 0–70° , rotation angle ß = 0–360°, angle step Δα = Δß = 5°. The ODF was calculated using X'Pert texture analytical software.

3. Results and discussion

3.1. The compositional phases and structure of $Co_{1-x}Pt_x$ (0.09<x<0.86) nanowire arrays

Fig. 1 shows the XRD pattern of as-deposited CoPt nanowires. Initially, two weak peaks, identified as $(10\bar{1}0)$ and $(11\bar{2}0)$ are

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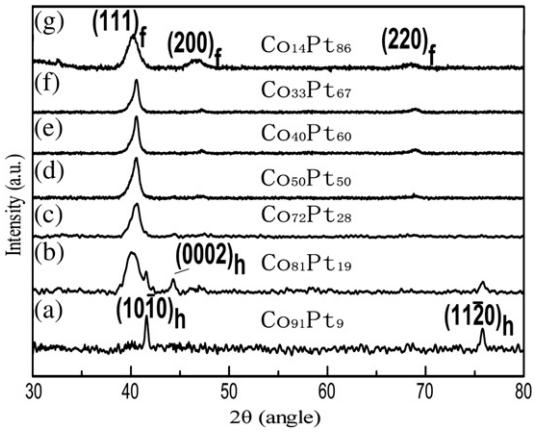

Fig. 1. X-ray diffraction patterns of the as-deposited nanowire arrays: (a) $Co_{91}Pt_9$, (b) $Co_{81}Pt_{19}$, (c) $Co_{72}Pt_{28}$, (d) $Co_{50}Pt_{50}$, (e) $Co_{40}Pt_{60}$, (f) $Co_{33}Pt_{67}$, and (g) $Co_{14}Pt_{86}$.

Table 1
Phase structure, lattice parameter, crystal plane orientation correction factor $T_{(111)}$, FWHM for (111) diffraction line and grain size $D_{(111)}$.

Composition (at.%)	Phase composed	lattice constant (Å)	$T_{(111)}$	FWHM (°)	$D_{(111)}$ (nm)
9	hcp ε-Co solid solution	a = 2.56, c = 3.90			
19	fcc α-Co,Pt solid solution + hcp ε-Co (minor)	a = 3.772	0.62	1.59	6.1
28	fcc α-Co,Pt solid solution + hcp ε-Co (trace)	a = 3.765	0.60	1.14	8.2
50	fcc Co,Pt solid solution	a = 3.768	0.46	0.91	10.3
60	fcc Co,Pt solid solution	a = 3.770	0.58	0.69	13.6
86	fcc Co,Pt solid solution	a = 3.777	0.60	1.36	6.9

observed with the $Co_{0.91}Pt_{0.09}$ alloy nanowires. With Pt content increasing to 19 at.%, relatively stronger (0002) reflection appears, implying that the primary hcp phase with magnetocrystalline easy axis (the <0001> direction) parallel to the wire axis.

At the Pt composition ranging from 19 at.% to 28 at.%, two weak peaks appear around 2θ = 41.2° and 44.6°. At the same time, the broadening of the (111) peak of the fcc $Co_{1-x}Pt_x$ solid solution (or fcc α-Co,Pt solid solution) [1] is observed , which indicates a significant distortion in the lattice during the transition from hcp to fcc phases. As the Pt content increases further, all trace of hcp ε-Co peaks vanish and the (111) reflection becomes more pronounced. With reference to the data in Fig. 1, it is interesting to note that nearly all the peaks positions at the Pt content from 19 at.% to 86 at.% shift slightly to a lower 2θ, which may be attributed to the formation of the α-Co,Pt solid solution, leading to a larger d spacing and hence to an expansion of the crystal lattice. The diffraction lines of the XRD patterns also become narrower when the Pt content increasing, which is attributed to the absence of the interface stress between hcp and fcc phase as only fcc Co,Pt solid solution existing. But broadening again at the highest Pt content, it is need to be further investigated. The comparatively low intensity of the hcp peaks could be indication of a small grain size or a high density of stacking faults [6] or caused by the X-ray fluorescence due to the Cu radiation.

Table 1 shows the grain size estimated from the XRD using the Scherrer equation:

$$B = k\lambda / D\cos\theta \quad (1)$$

where B is the full-width at half maximum (FWHM in the 2θ scan, k is a constant(0.94) , λ is the X-ray wavelength, D is the grain size, and θ is the angle of the diffraction peak. The grain sizes range from 6 to 14 nm. The grain size is only 6.1 nm for the Pt at 19 at.%, it is sufficiently small to result in peak broadening. These results agree with previous report for electrodeposited $Co_{1-x}Pt_x$ thin films [2]. From Table 1, it can be seen that the crystal structure developed progressively from the disordered hcp ε-Co solid solution (9 at.% Pt) to a mixture of the disordered fcc α-Co,Pt solid solution and minor ε-Co (19–28 at.% Pt) , finally moving to pure fcc Co,Pt solid solution. More extensive structure parameters obtained from the Rietveld refinement analysis, including lattice constant of the main phase and texture correction factor, are also listed. Fig. 2(a) and (b) shows the observed and calculated profiles for samples with x = 50 and 86 at.% Pt, where the R_{exp} is employed to evaluate the quality of the fitting. The fitting is good when it is under the 10.The lattice parameter coming from refinement is in agreement with a previous experimental report [1,3]. The Rietveld refinement assumes grain in a sample with an ideally random orientated distribution. However, in practice the sample is unlikely to be perfect orientation averaged for such a

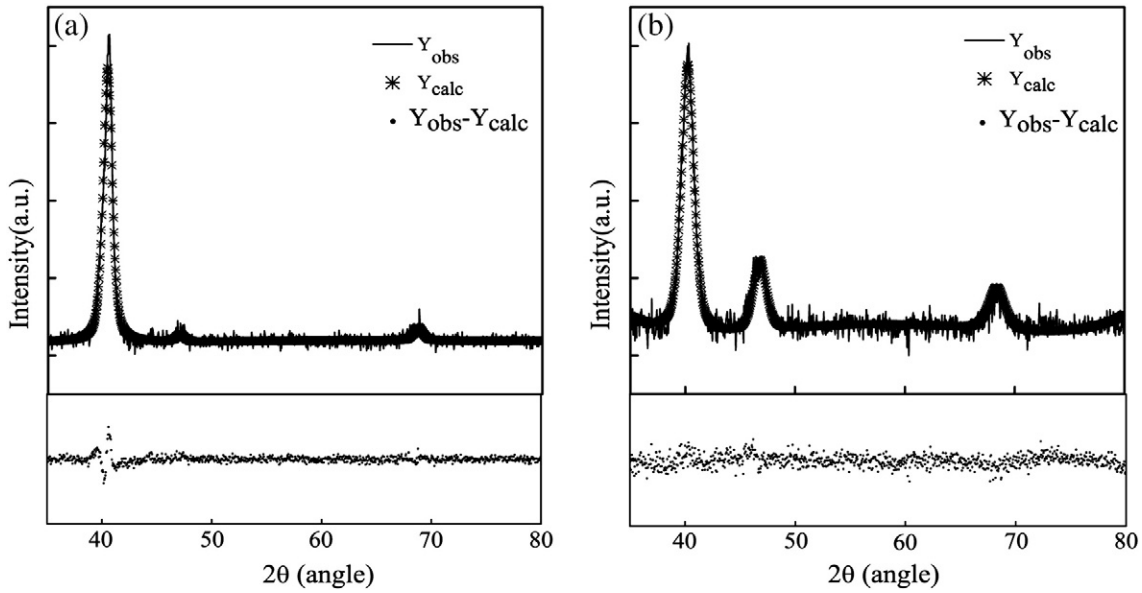

Fig. 2. Observed (solid lines) and calculated (star points) X-ray diffraction patterns for CoPt with content (a)50 at.% Pt and (b)86 at.% Pt. The dots at the bottom of each panel show the difference. $R_{exp} = 6.3$.