

CoPt–C nanogranular magnetic thin films

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Cobalt–platinum–carbon thin film was deposited with a chemical composition of $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$. The film had a nanogranular morphology with a grain size ranging from 5 to 15 nm. It consisted of cobalt–platinum grains which had a faulted hexagonal close-packed phase and were separated by graphitelike carbon boundaries. The film in-plane coercivity was 1500 Oe, compared to a few hundreds oersteds in the case of cobalt–carbon. This result establishes a way of fabricating high coercivity cobalt–carbon based materials, which have potential applications as high density magnetic recording media. © 1997 American Institute of Physics. [S0003-6951(97)04049-7]

High density magnetic recording media, with an areal density in the range of 10 Gb/in.², primarily require high coercivity and low-noise media.¹ High coercivity is essential to increase the linear resolution of the media; it should be in the order of 2000 Oe. Reduction of the media noise is usually obtained via magnetic isolation of the media grains; this weakens or eliminates the exchange coupling between the grains. In order to magnetically isolate the grains different solutions have been proposed such as physical separation of the grains² and segregation of a nonmagnetic phase at the grain boundaries.^{3–5} One of us proposed nanogranular Co–C thin film as a new candidate for high density recording media.⁵ The Co–C thin film consists of nanograins of cobalt embedded in graphitelike carbon. The film microstructures were analyzed as a function of the carbon concentration, the substrate temperature, and subsequent annealings.⁶ Although the Co–C nanogranular morphology seems to be very promising for applications requiring low-noise media, the film coercivity remains too low, typically a few hundred oersteds when the cobalt grains are 10 nm in size. In this letter, we report on the addition of platinum to the Co–C films, which results in high-coercivity CoPt–C films.

The film deposition technique was similar to the one previously reported,^{5,6} but a platinum plate was added onto the cobalt target. The Pt concentration was controlled by changing the position of the Pt plate on the Co target. The reported data have a Pt concentration of $\text{Co}_{76}\text{Pt}_{24}$, as determined by x-ray fluorescence analysis. The carbon concentration was determined by Auger electron spectroscopy. The chemical composition of the film was $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$. A film without Pt was deposited for comparison purposes; its chemical composition was $\text{Co}_{60}\text{C}_{40}$. The substrate temperature was 250 °C and the deposition rate was 5 nm/min for both films.

Cleaved NaCl crystal and glass substrates were used. A carbon underlayer, 10 nm thick, was first deposited. Then the CoPt–C film was deposited, the thickness of which was 30 nm. The film on the NaCl was floated in purified water, and the resulting free-standing thin film was put onto a holey carbon film supported by a copper mesh, which was used in transmission electron microscopy (TEM) analysis. Gold par-

ticles were used to calibrate the position of the rings in the electron diffraction pattern. The as-deposited films were subsequently annealed at $T_a = 350$ °C for 1 h in a vacuum (the pressure was less than 10^{-6} Torr). The following results relate to the annealed films. The film microstructure was analyzed using TEM and selected area diffraction (SAD) pattern. The magnetic hysteresis curve was measured with a vibrating sample magnetometer (VSM) on the glass substrate samples.

Low-magnification TEM plane views and SAD patterns of Co–C and CoPt–C films are shown in Figs. 1(a) and 1(b), respectively. The TEM plane views show that Co–C and CoPt–C films had a similar morphology; the grain size of Co–C and CoPt–C ranged from 8 to 25 nm and from 5 to 15 nm, respectively. From this grain size difference, broader rings in the SAD of CoPt–C are expected. The results of the determination of the phases and d -spacing values from the SAD patterns are reported in Table I. The Co–C diffraction pattern of Fig. 1(c) can be indexed as the hexagonal close-packed (hcp) Co phase, small intensity spots which corresponded to the (200) face-centered cubic (fcc) Co plane and a broad graphite (00.2) ring. No apparent crystal texture was observed. As Table I and Figs. 1(c)–1(d) show, the addition of Pt in the concentration $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ resulted in: (1) a shift of d spacings toward larger values; (2) a broadening of $(10.1)_{\text{hcp}}$, $(10.2)_{\text{hcp}}$, and $(10.3)_{\text{hcp}}$, the two latter had a very weak intensity; and (3) the $(200)_{\text{fcc}}$ spots found in Co–C could not be detected in the case of CoPt–C.

It is known that CoPt bulk alloy forms a complete solid solution,⁹ and that Pt mixing in carbon is less than 1 at. %. Also the lattice parameters of CoPt alloy increase with the Pt concentration. As Table I shows, the expansion of the d spacings of the CoPt hexagonal phase amounted to 2%. Assuming that Vegard's law has a linear dependency between the $(00.2)_{\text{hcp}}$ Co and $(111)_{\text{fcc}}$ Pt planes, the $(00.2)_{\text{hcp}}$ CoPt d spacing at a Pt concentration of 24 at. % is estimated to be 2.09 Å, which is close to the measured d spacing of 2.08 Å. This suggested that CoPt alloy was formed and that segregation of Pt was not very important. The broadening of the (h,k,l) rings, fulfilling the condition $h - k = 3n \pm 1$, where n is an integer and l not 0, is an indication of a faulted hcp phase.⁸ Indeed stacking faults were observed in TEM high resolution plane view. At 24 at. % Pt, the $(200)_{\text{fcc}}$ spots could not be detected. Two explanations can be proposed:

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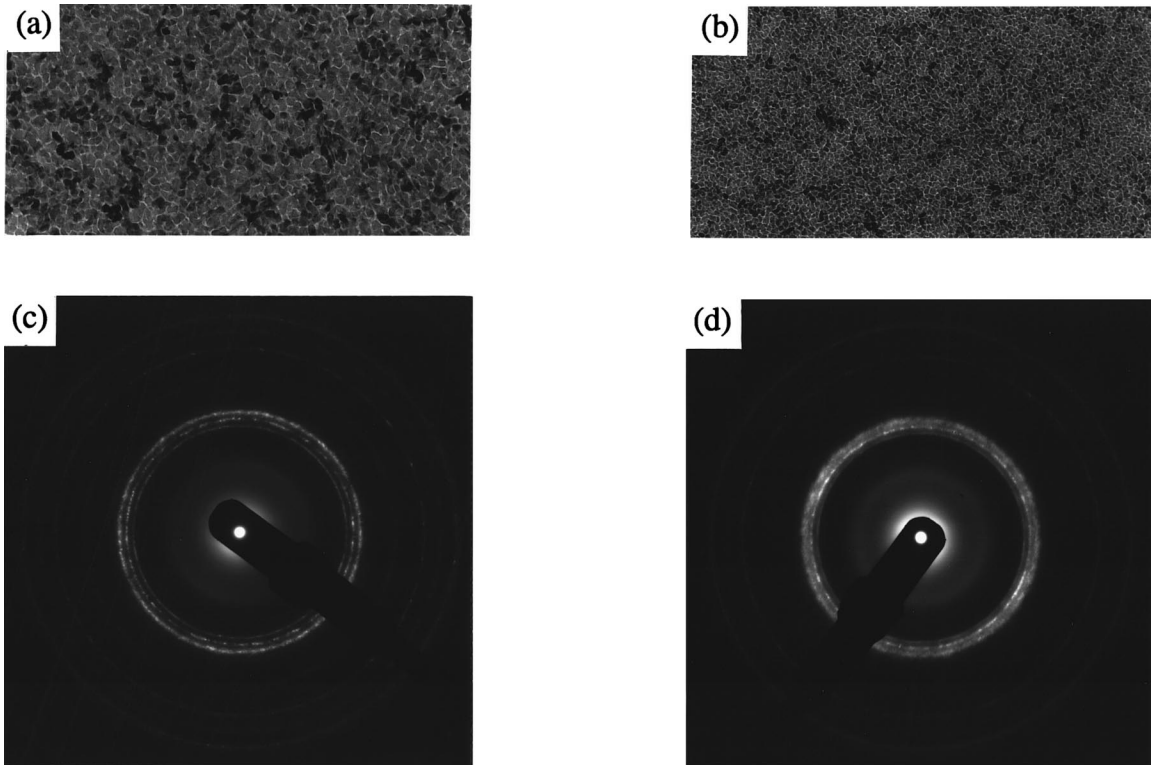


FIG. 1. Low-magnification TEM plane views of (a) $\text{Co}_{60}\text{C}_{40}$ and (b) $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ films and their corresponding SAD patterns (c) and (d).

(1) as shown by the CoPt phase diagram,⁹ the addition of Pt increases the phase transition temperature from hcp to fcc, thus it should prevent the formation of the fcc phase; (2) the $(200)_{\text{fcc}}$ spots may not be observed because of the very small size of the fcc phase and/or its lack of crystal quality.¹⁰ A detailed study of the crystal structure of CoPt using high resolution TEM is necessary to address this problem. In the $\text{Co}_{75}\text{Pt}_{25}$ alloy reported in Ref. 11, the fcc phase is clearly observed in the SAD pattern, unlike in our results. Reference 10 discusses a $\text{Co}_{73}\text{Cr}_{15}\text{Pt}_{12}$ alloy that had a hexagonal phase with local fcc stacking as observed in high resolution TEM image, but the contribution of the fcc phase to the SAD was not detected when the density of fcc stacking was low. Our case may be similar. We conclude that adding 15 at. % Pt to Co-C reduced the amount of fcc in the Co phase.

A TEM plane view of $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ showing details of the film morphology is given in Fig. 2. A granular morphology is observed. The dark regions of the grains correspond to the

hcp CoPt phase and the bright regions of the grain boundaries correspond to the graphitelike C phase. The grain size ranged from 5 to 15 nm, and the separation regions between the grains were about 2 nm thick.

Figure 3 shows the in-plane magnetic hysteresis loop of the CoPt-C film. The film plane is an easy plane. The coercivity H_c was 1500 Oe, the saturation magnetization M_s was 650 emu/cc, and the squareness S was 0.6. The results of the $M-H$ loop measurements of Co-C and CoPt-C films, annealed at 350 and 400 °C, are reported in Table II. The coercivity increased from 550 to 1500 Oe when the Pt concentration varied from 0 to 15 at. %, at $T_a = 350$ °C. The

TABLE I. The d -spacing values as obtained from the SAD patterns of Co-C and CoPt-C films. The accuracy of the measured d -spacing values was ± 0.01 Å.

| Plane | Co bulk ^a d spacing (Å) | $\text{Co}_{60}\text{C}_{40}$ d spacing (Å) | $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ d spacing (Å) |
|-----------------------|---|--|--|
| (002) graphite | | ~3.3 | ~3.5 |
| (10.0) _{hcp} | 2.165 | 2.17 | 2.22 |
| (00.2) _{hcp} | 2.030 | 2.04 | 2.08 |
| (10.1) _{hcp} | 1.910 | 1.91 | ~1.94 |
| (200) _{fcc} | 1.772 | 1.78 | weak (?) |
| (10.2) _{hcp} | 1.482 | 1.48 | weak |
| (11.0) _{hcp} | 1.252 | 1.25 | 1.28 |
| (10.3) _{hcp} | 1.148 | 1.16 | weak |

^aSee Ref. 7

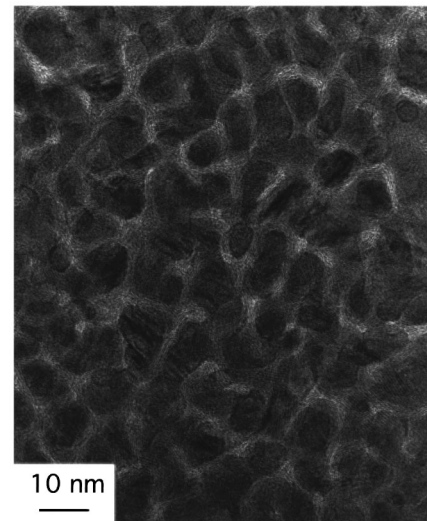


FIG. 2. In-plane bright field TEM image of $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ film showing a granular morphology. The film thickness was 30 nm.

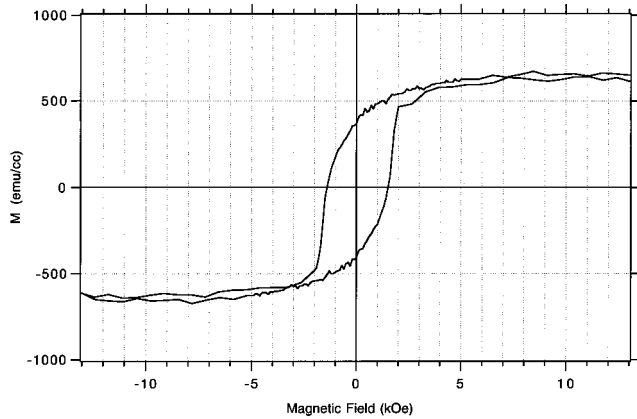


FIG. 3. In-plane magnetic hysteresis loop of $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ film.

saturation magnetization of Co-C film increased significantly when T_a was increased from 350 to 400 °C, whereas M_s of CoPt-C did not increase significantly. Fully transformed Co-C upon annealing had a larger M_s than that of CoPt-C.

The increase in coercivity on the addition of 15 at. % Pt may be related to an increase in the magnetocrystalline anisotropy of the CoPt alloy compared with that of the Co phase. Particularly if, on the addition of Pt, the Co fcc phase formation is suppressed, the magnetocrystalline anisotropy

TABLE II. Saturation magnetization M_s , coercivity H_c , and squareness S as obtained from the in-plane M - H loop of the Co-C and the CoPt-C films for the annealing temperature T_a of 350 and 400 °C.

| Grain size (nm) | $\text{Co}_{60}\text{C}_{40}$ | | $\text{Co}_{50}\text{Pt}_{15}\text{C}_{35}$ | |
|-----------------|-------------------------------|-----|---|------|
| | 8-25 | 400 | 5-15 | 400 |
| T_a (°C) | 350 | 400 | 350 | 400 |
| M_s (emu/cc) | 650 | 800 | 650 | 700 |
| H_c (Oe) | 550 | 450 | 1500 | 1600 |
| S | 0.65 | 0.6 | 0.6 | 0.55 |

of CoPt should be larger than that of Co. The fcc Co magnetocrystalline anisotropy is one order smaller than that of hcp Co. However the reason for an increase in H_c with Pt is not clearly understood, and conflicting reports can be found in the literature.^{10,11} In the CoPt alloy case of Ref. 11, the formation of local fcc stacking is interpreted as a factor that increases H_c . In the CoCrPt alloy,¹⁰ however, the changes in the crystal structure on the Pt addition are not related to an increase in H_c .

In conclusion, nanogranular CoPt-C film consisting of CoPt grains separated by a graphitelike C phase was fabricated. The film coercivity was 1500 Oe at 15 at. % Pt for an annealing temperature of 350 °C. This result established a way to fabricate high-coercivity Co-C base materials. The coercivity of CoPt-C was much improved compared to that of Co-C, but improvements are still required in order to realize a practical high areal density media. The addition of Pt modified the crystal structure of the Co grains by expanding the lattice constants and reducing the proportion of the fcc phase. Investigations of the CoPt-C film physical properties such as crystal structure and electronic state will be necessary to determine the reason for the high coercivity observed.

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