Magnetic Metal Alloy-Carbon Nanocomposite Thin Films by Pulsed Filtered Vacuum Arc Deposition

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Abstract CoPt-C, FePt-C and PrCo-C nanocomposite thin films were prepared by a pulsed filtered vacuum arc deposition technique. Vacuum thermal annealing and rapid thermal annealing were performed at various temperatures. The dependence of the magnetic properties on the carbon fraction and annealing temperature was studied. For the film with a particular composition of Fe_{43}Pt_{35}C_{22}, the coercivity and the grain size were observed to increase with increasing annealing temperature, up to a value of 3.5 kOe at an annealing temperature of 650°C, and with a grain size about 10.5 nm. For the sample of (Pr_{0.17}Co_{0.83})_{69}C_{31} annealed at 700°C for one minute, it showed a large coercivity of 5.2 kOe and a small grain size of 7.8 nm. The overall small negative $\Delta M$ of this film indicated that virtually all the Pr$_{0.17}$Co$_{0.83}$ grains were isolated single domain particles with only weak dipolar interactions among them. These results indicated that these nanocomposite thin films would be promising candidates for high-density magnetic recording medium applications.

Key words: high-density magnetic recording, high $K_u$ materials, granular films, ferromagnetic.
1. Introduction

The rapid progress and significant improvement in magnetic information storage systems over the past few years have led to intensive research efforts in search of extremely high-density recording (EHDR) media with an area density of 100 Gb/in² or higher. In order to have low medium noise, EHDR media would need to have a coercivity ($H_c$) of about 4 kOe and weakly exchange-coupled grains of less than 10 nm in size according to very simple estimates [1].

For such a small grain size, the issue of thermal stability must be considered. In the Stoner–Wohlfarth model, for a medium with particle volume $V$ and uniaxial anisotropy constant $K_u$ at temperature $T$, it is usually required to have

$$K_u V/k_B T > 60 \quad (1)$$

in order for the medium to be thermally stable. For grain size d-10 nm, $K_u > 2 \times 10^5 \text{erg/cm}^3$ is required from Eq.(1). CoPt and FePt in the face-centered tetragonal (fct) phase and PrCo$_2$ have large $K_u$ values of about $10 \times 10^5 \text{erg/cm}^3$, $5 \times 10^7 \text{erg/cm}^3$, $6.6-10 \times 10^7 \text{erg/cm}^3$, respectively [2]. Therefore all of them are good candidate materials for applications in ultra high recording media [1-3].

Recently, carbon encapsulated magnetic nanograins have been intensively studied [4-7]. The most important advantage of carbon encapsulation is the increase of the effective distance of neighboring magnetic grains so that the inter-grains exchange coupling can be weakened or eliminated. This is an important issue for the reduction of media noise. On the other hand, all of the CoPt, FePt, PrCo$_2$ and C phases have excellent chemical stability and good corrosion resistance. Carbon encapsulation can also provide protection for air-sensitive grains against degradation. In this work, we have employed the pulsed filtered vacuum arc deposition technique to prepare CoPt-C, FePt-C and PrCo-C nanocomposite films of various carbon compositions and studied their properties.

2. Experiments

CoPt-C, FePt-C and PrCo-C nanocomposite thin films of about 30 nm to 50 nm thick of various compositions were prepared by a 3–source pulsed filtered vacuum arc deposition system. The details of the system have been described elsewhere [7]. Three adjacent sources with pure graphite, platinum and cobalt or iron or praseodymium as the cathode materials were operated simultaneously in a pulse mode with a pulse duration of 2.5 ms. Of the three sources, the platinum source was positioned at the center. The substrate was placed at the center of the chamber facing the platinum source and a negative bias voltage of -80 V was applied. The composition of the films was varied by adjusting the arc discharge conditions and was monitored by the integrated charges arriving at the sample holder from the respective arc sources. Thermal annealing was performed in a vacuum furnace (<10$^{-3}$ Pa) at various temperatures $T_{\text{an}}$ for one hour for CoPt-C and for half an hour for FePt-C, respectively. For PrCo-C films, annealing was performed in argon atmosphere for one minute at $T_{\text{an}}$ ranging from 600°C to 850 °C. The composition and thickness of the CoPt-C, FePt-C and PrCo-C films were determined quantitatively by non-Rutherford backscattering spectrometry (NRBS) using a 2MV tandem accelerator. The structural properties were analyzed by x-ray diffraction (XRD). The magnetic properties were characterized by a vibrating sample magnetometer (VSM).

3. Results and discussion

There are two phases of CoPt and FePt, namely, face centered-cubic (fcc) and face-centered-tetragonal (fct) phases. The fct phase is known to have a larger $K_u$ value [1-3]. In order to obtain the ordered fct phase from disordered as-deposited fcc phase, high-temperature annealing is required to
overcome the energy barrier for superlattice ordering [1-4].

Figure 1. XRD patterns: (a) Co$_{24}$Pt$_{31}$C$_{45}$ films annealed at various temperatures in vacuum for 1 h. (b) Fe$_{43}$Pt$_{35}$C$_{22}$ films annealed at various temperatures in vacuum for 0.5 h. (c) (Pr$_{0.17}$Co$_{0.83}$)$_6$Co$_{31}$ thin films annealed at various temperatures as indicated for one minute.

Figure 1 (a) and (b) shows the XRD patterns of a Co$_{24}$Pt$_{31}$C$_{45}$ and a Fe$_{43}$Pt$_{35}$C$_{22}$ film annealed at various temperatures, respectively. The XRD patterns for fcc phase and nano-crystallites of fct phase are quite similar except that there are several additional peaks such as, fct (001) and fct (110) peaks for the fct phase [1]. The other peaks in the XRD patterns can be contributed by both the fcc and fct phases. As shown in Fig. 1(a), broad fct (001) and fct (110) CoPt peaks first emerged in the spectrum of the sample annealed at 600°C. This is an indication of the formation of the fct CoPt phase. These two peaks became sharper as $T_{an}$ increased to 650°C, indicating larger fct CoPt grains were formed. On the other hand, the fct (001) FePt peak is also observed in Fig. 1(b) in the spectrum of the sample annealed at 600°C indicating the formation of the fct FePt phase. The shaper fct (001) peak and the appearance of fct (002) peak in the spectrum of the 650°C annealed sample in Fig. 1(b) are indications of more complete phase transformation to fct FePt. The XRD patterns of PrCo-C film annealed at various temperatures for one minute are shown in Fig. 1(c). It is well known that PrCo can crystallize in three phases [8], namely, the PrCo$_7$ phase, the Pr$_2$Co$_{17}$ phase and the PrCo$_5$ phase. The (Pr$_{0.17}$Co$_{0.83}$)$_6$Co$_{31}$ thin film in this study was found to crystallize only in the PrCo$_5$ single phase. As $T_{an}$ increases, the XRD peak width corresponding to the PrCo$_5$ phase decreases, showing that the grain size in these films increases.

Figure 2a shows the in-plane (//) magnetic hysteresis loops of the Co$_{24}$Pt$_{31}$C$_{45}$ films after annealing at various temperatures in vacuum as indicated. These hysteresis loops for the Fe$_{43}$Pt$_{35}$C$_{22}$ films are shown in Figure 3b. For comparison, we have also included in each of these two graphs a perpendicular (\perp) magnetic hysteresis loop for the sample annealed at 650°C. It is seen from Figure 2a that as the annealing temperature increases, there is no significant change in the saturation magnetization of the films at a value of about 0.35 emu/cm$^3$. The film showed a soft ferromagnetic characteristic after annealing at 550°C with a coercivity of about 100 Oe and a saturation magnetic field of about 200 Oe. After annealing at a higher temperature of 600°C, the film became magnetically harder exhibiting a coercivity of 760 Oe. The increase in coercivity is attributed to the formation of the fct CoPt phase.
The coercivity increased further with increasing $T_{an}$ up to a value of 2.5 kOe at $T_{an} = 700^\circ$C. This is also understandable to be the result of fct CoPt grain growth and more complete fcc to fct CoPt phase transformation.

![Figure 2](image_url)

**Figure 2.** In-plane (//) and perpendicular (⊥) magnetic hysteresis loops measured at 300 K for the samples: (a) Co$_{24}$Pt$_{31}$C$_{45}$, (b) Fe$_{43}$Pt$_{31}$C$_{22}$ and (c) (Pr$_{0.17}$Co$_{0.83}$)$_{69}$C$_{31}$ films after annealing at the temperature as indicated.

As shown in Figure 2b, the Fe$_{43}$Pt$_{31}$C$_{22}$ films have a larger saturation magnetization value of about 1000 emu/cm$^3$. The coercivity is observed to increase with increasing $T_{an}$ up to a value of 3.5 kOe at $T_{an} = 650^\circ$C with an squareness ratio of 0.629. It is also seen that the ⊥ hysteresis loops show smaller coercivity and remanence values compared to their // counterparts.

Figure 2c shows the room temperature magnetic hysteresis curves of (Pr$_{0.17}$Co$_{0.83}$)$_{69}$C$_{31}$ films. The coercivity first increases with $T_{an}$ up to a maximum value of 12 kOe at $T_{an} = 750^\circ$C and then decreases with further increase in $T_{an}$.

Shown in Figure 3a is the grain size d against annealing temperature for the CoPt-C and FePt-C films of various compositions as indicated. The grain size was estimated by the Scherrer's formula using the (111) peak width for the CoPt-C films and the (001) peak width for the FePt-C films from the XRD patterns. The grain size of the films generally increases with $T_{an}$ due to thermal growth of the grains. It is also seen that higher carbon content for the CoPt-C films will result in smaller as-deposited grain size as well as suppression of grain growth upon annealing. In fact, XRD results also showed that for the film with the highest carbon content in this study, Co$_{19}$Pt$_{32}$C$_{60}$, the fct phase were observed only after annealing at temperatures equal or higher than 700$^\circ$C.

Figure 3b shows coercivity measured at 300 K against annealing temperature for the films with different composition as indicated. As $T_{an}$ increased, the coercivity of the films increased due to more complete fcc to fct phase transformation. However, for the Co$_{27}$Pt$_{31}$C$_{12}$ film, the coercivity increased with $T_{an}$ from 500$^\circ$C to 600$^\circ$C, and then decreased at 650$^\circ$C, even though it had the highest CoPt concentration. As $T_{an} = 650^\circ$C, the coercivity of the Co$_{27}$Pt$_{31}$C$_{12}$ film was measured to be only about 500 Oe, smaller than that of the Co$_{27}$Pt$_{31}$C$_{45}$ film, which exhibited a coercivity of about 2100 Oe, though the XRD patterns of both films showed the formation of fct CoPt phase. This is probably because the carbon content of the Co$_{27}$Pt$_{31}$C$_{12}$ film is too small to provide sufficient and effective encapsulation of the CoPt grains. Hence, the grain size grew rapidly with increasing $T_{an}$ up to 21 nm at 650$^\circ$C, causing the formation
of multi-domain structures in the film. In contrast, the film with the highest carbon content, CoPt35C50, exhibited the smallest coercivity. This is obviously correlated with the small amount of effective fct CoPt phase precipitated in this sample as inferred from the XRD results.

These results show that the grain size and coercivity strongly depend on the carbon content as well as thermal treatment conditions. On the other hand, the Fe30Pt35C22 film shows the largest the coercivity of 3.5 kOe and a grain size of 10.5 nm at $T_{an} = 650^\circ$C, which is quite close to the EHDR required values.

As shown in figure 3c are the average grain sizes $d$ of the (Pr0.17Co0.83)60C31 films annealed at various $T_{an}$ estimated using the Scherer's formula. The average grain size of these thin films with $T_{an} = 600^\circ$C, 700$^\circ$C, 750$^\circ$C, 800$^\circ$C and 850$^\circ$C were estimated to be 4.2 nm, 7.8 nm, 11.1 nm, 15.3 nm and 19.9 nm, respectively.

Figure 4 shows a TEM plane-view bright-field micrograph of the 700$^\circ$C annealed (Pr0.17Co0.83)60C31 film. The grain size is seen to be in the typical range of 5-10 nm.

![Figure 4. A TEM plane-view bright-field micrograph of the (Pr0.17Co0.83)60C31 film annealed at 700$^\circ$C.](image)

The coercivities of (Pr0.17Co0.83)60C31 films determined from Figure 2c are plotted in Figure 3c. The corresponding estimated grain size is about 11 nm for the sample with $T_{an} = 750^\circ$C, which has the largest coercivity of 12 kOe. Both the coercivity value and the grain size of this sample are a bit too large for applications as EHDR media. However, the sample with $T_{an} = 700^\circ$C is attractive for this application. It showed an average grain size 7.8 nm and a coercivity of 5.2 kOe, well matched the requirements for EHDR applications.
Besides the coercivity and grain size, another important issue of concern for application as EHDP media is the exchange coupling between the magnetic grains. It is desirable that the exchange coupling between magnetic grains in magnetic nanocomposite films could be weakened or eliminated by the separation of the non-magnetic matrix, hence resulting in magnetic isolated grains. The $\Delta M$ curve measurement, which is obtained from the isothermal remanence (IRM) and the dc demagnetization (DCD) curves, is a common method to directly obtain information about the magnetic intergranular interaction [9]. Figure 5a shows the IRM curve and DCD curve at room temperature for the sample with $T_{an} = 700^\circ$C.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{(a) IRM curve and DCD curve at room temperature for the (Pr$_{0.17}$Co$_{0.83}$)$_{60}$C$_{31}$ annealed at 700$^\circ$C. (b) The $\Delta M$ curve at room temperature for the same sample as in (a).}
\end{figure}

$\Delta M$ is defined as $m_T(1-2m_s)$, where $m_T$ and $m_s$ are the reduced dc remanence and isothermal remanence, respectively [9]. For non-interactions single domain particles, $\Delta M = 0$. A positive $\Delta M$ indicates intergranular exchange coupling and a negative value indicates a long-range dipolar interaction. Figure 5b shows the $\Delta M$ curve for the sample with $T_{an} = 700^\circ$C. The overall small negative $\Delta M$ indicates that virtually all the Pr$_{0.17}$Co$_{0.83}$ grains in the film were isolated single domain particles with only a small amount of dipolar interactions between them.

4. Conclusion

In summary, we have successfully prepared nanocomposite CoPt-C, FePt-C and PrCo-C thin films. Relatively large coercivity and considerable small grain size were observed in these films. For the film (Pr$_{0.17}$Co$_{0.83}$)$_{60}$C$_{31}$ annealed at 700$^\circ$C for one minute, it was shown to be chemically stable, exhibits a coercivity value of 5.2 kOe, an average grain size 7.8nm, and only weak dipolar interactions between magnetic grains. These properties are highly desirable for extremely high-density magnetic recording medium applications.

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Reference