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LETTER TO THE EDITOR

EVIDENCE OF PHOSPHOROUS SEGREGATION IN GRAIN BOUNDARIES IN ELECTROLESS-PLATED Co–P THIN FILM

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Co thin films prepared by an electroless deposition technique were analyzed by X-ray energy dispersive spectroscopy in the transmission electron microscope. The overall composition of the deposited film was determined to be approximately Co–4.1 wt%P (Co–7.5 at%P). The spectra taken from the center of the individual grains did not show any evidence of phosphorous. However, when the electron beam was located at the triple point of grain boundaries, a phosphorous peak was detected. Thus, this establishes that the grains are essentially pure Co and that the phosphorous is significantly segregated to the grain boundaries. This may be the cause of the magnetic isolation of the grains.

1. Introduction

Co base alloy thin films are promising candidates for high density magnetic recording media. Among these, Co–P and Co–Ni–P alloy thin films can be prepared by the chemical deposition technique, which makes them particularly attractive for commercial application since the deposition rate is much faster than the other methods. It is well known that the magnetic properties of these films strongly depend on the microstructure features such as grain size, film thickness and crystallographic texture [1–5]. The microstructure is controlled by the deposition conditions such as the pH and temperature of the plating bath. Hence, there are several detailed studies which correlate the magnetic properties and the deposition conditions [4,5].

According to the previous studies [4,5], a unique feature of the microstructure of the Co–P thin films prepared by means of electroless deposition is the existence of the so called "channels". In the bright field transmission electron microscopy (TEM) image, the grain boundaries display bright channel-like contrast which appears to isolate individual grains. Such a unique microstructure was reported for films with a high coercivity [4]. Also the grain size of these films is reported to be in the range of a few tens of nanometers [4,5], which is close to the critical diameter for single domain formation of Co particle [6]. Hence, a particulate model has been generally accepted for Co–P films. To our knowledge, however, no attempt has been made to prove directly that phosphorous is segregated to the grain boundaries, which would magnetically isolate the individual grains. Although the segregation of phosphorous to the grain boundaries seems to be a reasonable assumption in view of the fact that there is essentially no solubility of phosphorous in cobalt [7], it is important to prove this experimentally.

The aim of this paper is to show direct evidence of phosphorous segregation to the grain boundaries of Co–P thin films using X-ray dispersive spectroscopy (EDS) in the transmission electron microscope (TEM).

2. Experimental

Co–P thin films used in the present study were kindly supplied by Alcoa Technical Center, PA. The Co–P magnetic thin films were deposited on formvar films that had been sensitized by a Sn–Pd solution. The bath solution contained approximately 1.6 g/l Co^{2+}, 12 g/l Na hypophosphite, 22

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Fig. 1. A typical bright field image of electroless deposited Co–P thin film and the corresponding selected area diffraction pattern.

g/l Na borate, 50 g/l citrate and 17 g/l glycine. The temperature of the bath was maintained at 71° C and the pH was 10. The sample examined in this study had a coercivity of 850 Oe.

The thin film samples were placed on Cu grids and observed in an analytical electron microscope, Philips EM420 using a LaB_6 filament. EDS analysis was performed in the TEM mode using a probe size which is estimated less than 20 nm. The count rate was somewhere between 25 to 15 cps and the data were collected for 100 s. For determining the overall alloy composition, a larger electron probe, ≈ 200 nm, was used. The data were semiquantitatively analyzed using the Cliff–Lorimer ratio method [8]. The details are discussed in the next section. Absorption correction and fluorescence correction are assumed to be negligible.

3. Results and discussions

A typical bright field TEM image is shown in fig. 1 together with a selected area diffraction (SAD) pattern. The SAD pattern displays all the hcp rings which are expected from the randomly oriented polycrystalline sample. This indicates that the orientation of the grains is more or less random, although a slight tendency to texture cannot be ruled out. The microstructure is typical of a Co–P thin film, i.e., the grains are very small and the grain boundaries display bright contrast (or channels) with respect to the grains. The question is whether or not those channels are enriched with phosphorous as suggested in the past studies [1–5]. In order to answer this question, three types of EDS spectra were taken. One was taken using approximately 200 nm electron probe, which gives overall alloy composition. The other two types

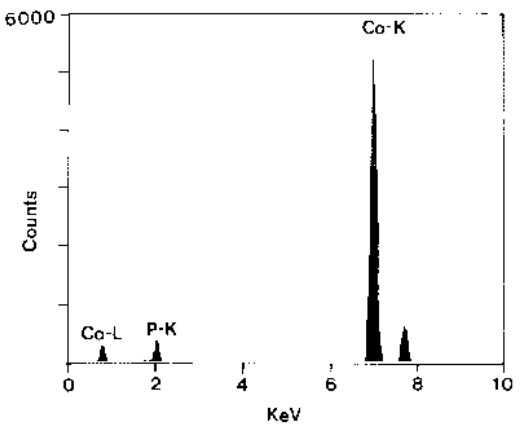

Fig. 2. EDS spectrum of Co–P thin film which was taken by using ≈ 20 nm electron probe. The overall phosphorous concentration was estimated to be ≈ 4.1 wt% (≈ 7.5 at%).

were taken using nominal < 20 nm electron probe. One was from the center of a large grain; the other was from the region which contains the triple point of the grain boundaries (or "channels").

The EDS spectrum of Co–P thin film obtained by using ≈ 200 nm electron probe is shown in fig. 2. This spectrum shows that the thin film is essentially a Co–P binary alloy. Strong Cu peaks were also observed in all spectra. Since they are believed to be due to the spurious X-ray from the copper grids, the copper peaks have been eliminated from the figure. The integral X-ray intensity ratios were converted to weight percent by multiplying by the Cliff–Lorimer factor [8]. The Cliff–Lorimer factor, k_{PCo}, was obtained from the table values in ref. [9] using the relation, $k_{PCo} = k_{PFe}/k_{CoFe}$. The composition of the alloy film was, hence, determined to be about Co–4.1 wt%P (Co–7.5 at%P). Note that the Cliff–Lorimer factor obtained from the table value may contain 10% uncertainty, since it is instrument dependent. Therefore the phosphorous concentration determined using this factor may contain some uncertainty. However, the aim of this study is not to determine the absolute concentration of phosphorous, but to decide whether or not phosphorous is segregated at the grain boundaries. Since the Cliff–Lorimer factor is constant throughout the analysis, the concentration determined by using a single value is meaningful for comparing the local concentration difference. Since the X-ray count rate was very small when such a probe size was used, a more important error is that due to counting statistics. This error was evaluated following the method described by Romig and Goldstein [10], i.e., the relative error in the number of counts, N, is $3N^{1/2}$ at the 99.7% confidence level. Hence, the phosphorous concentration is determined to be (4.1 ± 0.3) wt%.

According to Hansen's phase diagram [7], there is essentially no solubility of phosphorous in cobalt. If this film is in the equilibrium state (which may not be necessarily true for deposited films), phosphorous cannot be dissolved in Co; hence phosphorous must exist as either Co_2P precipitates or P enriched regions. Since no evidence of Co_2P was found by electron diffraction, it is most probable that P simply segregates to the grain boundaries without forming the Co_2P compound.

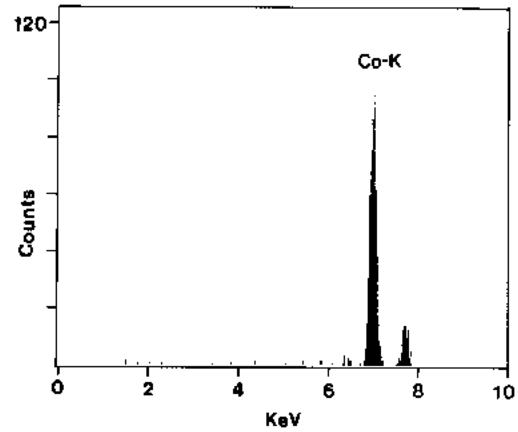

Fig. 3. EDS spectrum taken from the center of a grain of a Co–P thin film. Note that no phosphorous peak was detected. The nominal probe size was less than 20 nm.

An EDS spectrum taken from a grain using nominal < 20 nm probe is shown in fig. 3. Although strong cobalt X-ray peaks are observed as in the case of fig. 1, no phosphorous peak is identified. After background subtraction, there was only one count which corresponds to phosphorous X-ray energy. Assuming that this count is not due to background noise, the phosphorous concentration determined with the same method as above is (0.1 ± 0.3) wt%. However, there is a possibility that the phosphorous signal was simply the background; in this case, the phosphorous concentration is zero. In any case, this result corresponds with the phase diagram which indicates that there is essentially no solubility of phosphorous in cobalt.

With the same spot size as above, EDS spectrum was obtained by locating the electron probe at the triple point of the grains, as shown in fig. 4. Different from fig. 3, a phosphorous peak is clearly identified. The composition of phosphorous was determined to be approximately (4.9 ± 1.4) wt%. Comparing this value with the overall composition, (4.1 ± 0.2) wt%, we cannot say there is a significant difference between those two values. As expected from the poor counting statistics, it is shown that phosphorous segregation is not detectable if the concentration is compared with the overall alloy composition. On the other hand, if the phosphorous concentration at the grain

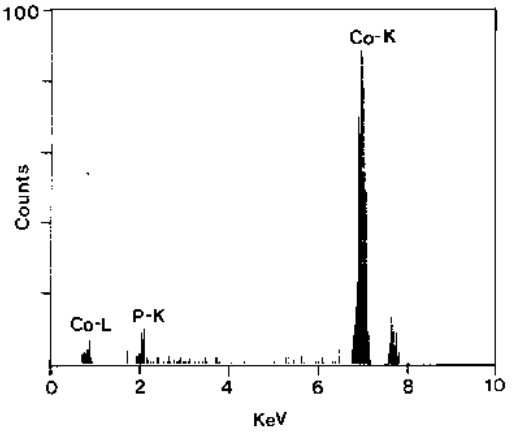

Fig. 4. EDS spectrum taken from the triple point of grain boundaries of a Co–P thin film. Note that the phosphorous peak is clearly observed. The probe size is exactly the same as that in fig. 3.

boundary region, (4.9 ± 1.4) wt%, is compared with that of grains, 0 to 0.4 wt%, the enrichment of phosphorous at the grain boundaries becomes evident. Therefore, we can conclude that phosphorous is segregated to the grain boundaries. Since the probe size is significantly larger than the grain boundary area, the phosphorous composition in the grain boundary must be much higher. From the noticeable channel-like contrast of Co–P grain boundaries, the segregated layer seems to extend further than single mono-layers. This might be the reason why the P segregation was detected even with the significantly larger probe size than the grain boundary region. Such brighter channel-like contrast in the bright field TEM image may be explained by the lower atomic-scattering factor of P.

Now that it has been shown that phosphorous segregates to the grain boundaries, it is easily conceivable that the grains are magnetically isolated by the existence of nonmagnetic phosphorous enriched layers. This justifies the particulate model to explain the magnetization of Co–P thin films. Indeed, our attempt to observe magnetic contrast by Lorentz microscopy was not successful. This result is consistent with the assumption that the isolated grains form single domains. Similar results were reported previously by Aspland et al. [4], in which they reported that no magnetic contrast was obtained if the coercivity of the films was higher than ≈ 450 Oe. The coercivity of the present film is 850 Oe, and the grain size is approximately 20 nm. Therefore, it is reasonable to conclude that the isolated particles are single domain and only magnetization rotation is possible.

4. Conclusion

EDS spectra taken from the center of the grains showed no phosphorous peak. On the other hand, EDS spectra taken from the area containing a triple point of the grain boundaries showed clear phosphorous peak. Since this film was found to contain 4.1 wt% of phosphorous overall, it is concluded that phosphorous was significantly enriched at the grain boundaries. This result justifies a particulate model of magnetization process of Co–P thin films.

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