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The Structure of Electroless Cobalt Films as Revealed by Electron Microscopy

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A brief survey, using transmission electron microscopy, of the crystallite structure of magnetic electroless cobalt films deposited from an alkaline hypophosphite bath on to glass substrates has been undertaken. With increasing pH values from 7.4 to 8.5, the overall continuity of the films improved for a given thickness, although the crystallites themselves became individually isolated. This isolation is responsible for the increase in coercivity observed over the same pH range. Micrographs of various specimens are included to illustrate the features discussed.

1. Introduction

Since its discovery by Brenner and Riddell [1], the technique of electroless deposition has been used frequently for the preparation of magnetic thin films. Specifically, thin films of cobalt have found application as recording tapes. The advantages of such films for this purpose are numerous: their thinness, high coercive force, high remanence, and squareness ratios approaching unity. Despite much attention, the magnetic reversal process still remains unclear, and consequently, as a prelude to this problem, we have undertaken a short study of the crystallite structure of these films. Most of the work has been accomplished with transmission electron microscopy, using in part the 500 kV machine of the University of Cambridge.

2. Experimental

All the films were prepared and supplied by ICT (Eng.) Ltd*. Basically, an alkaline hypophosphite bath of the type described by Fisher and Chilton [2] was used, in which the pH value and temperature could be easily varied. All the films were deposited on to glass substrates. They were removed from their substrates by briefly dipping them into dilute nitric acid, and then floating them off in water. The action of the acid was to start the film lifting from the substrate, and once this had started the film detached itself completely in water.

The films were examined using an EM6 microscope operating at 100 kV, and occasionally the 500 kV machine at the University of Cambridge.

The main variation of magnetic properties with preparation conditions is that of coercivity with pH. In the pH range 7.4 to 8.5 the film coercivities are high (i.e. ~ 250 Oe) and increase with increasing pH.

3. Results and Discussion

3.1. Crystallite Structure

Firstly, we shall discuss the electron diffraction results. All the specimens were crystalline (of coercivity in the range 300 to 700 Oe) and showed the same diffraction pattern, an example being given in fig. 1a. The rings, with an occasional exception, were consistent with an hcp phase: the origin of extraneous reflections has not been determined but the presence of cubic cobalt as a possible source was eliminated. In contrast, the recent work by Marton and Schlesinger [3] has confirmed the fact that electroless nickel/phosphorus films can be amorphous with a liquid-like diffraction pattern.

Moreover, no appreciable preferred crystallite orientation of any kind was observed: the pattern remained the same for specimen tilts of up to 10° about the axis of the microscope. Previous authors, using X-rays, have detected preferred orientations in which the *c*-axis was

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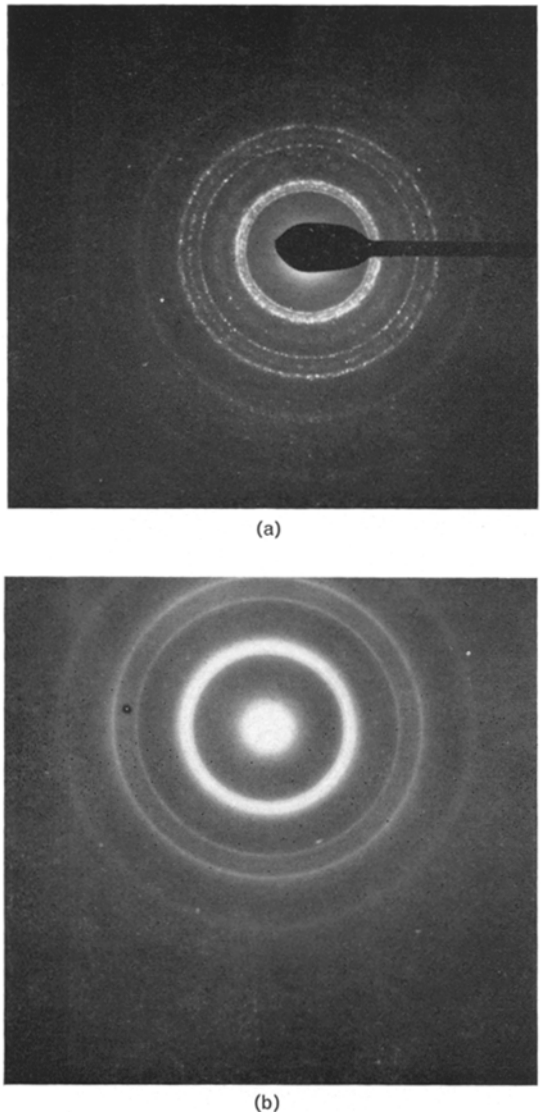

Figure 1a, b Diffraction patterns of electroless and evaporated cobalt.

either perpendicular [4] or parallel [5] to the film plane. For sake of comparison, we include in fig. 1b the diffraction pattern of an evaporated film of cobalt in which cubic reflections were detected. Clearly, the (002) reflection is comparatively strong, implying an arrangement whereby the c-axis preferred to be in the film plane.

In order to make as logical a discussion as possible, we shall concentrate on the two most important parameters of the deposition (apart from temperature), namely the pH value and film thickness. Below a nominal thickness of 400 Å none of the specimens was continuous. Rather, the films consisted of isolated groups of crystallites, as seen in fig. 2, where the thickness was 200 Å and the pH value was 7.7. Two general remarks can be made. First, the groups were separated by comparatively large regions of bright contrast which gave an amorphous diffraction pattern. These regions may have consisted of a thin layer from the activating solution introduced during the plating process. Second, there was a range of contrast within the separate colonies which enabled discrete crystallites to be identified. This variation could be due to two sources, diffraction contrast, i.e. crystallites in different orientations, and local changes in thickness.

Fig. 3, taken at 500 kV, is also of a low pH value film but of considerably increased thickness, *viz* 1000 Å. Clearly, similar features were observed, and, significantly, the film was still barely continuous. Overall, the film surface must have been extremely rough.

We consider next samples in the intermediate pH value range 7.8 to 8.2, an example being illustrated in fig. 4 (thickness = 500 Å, pH = 8). Although gradations in contrast remained, a greater continuity was evident even at this fairly low thickness. Moreover, a new and curious aspect emerged in that the crystallites tended to be isolated one from another by a series of channels of width 50 to 100 Å. Finally, in this range of pH values the amount of subcrystallite fine structure reached a maximum,

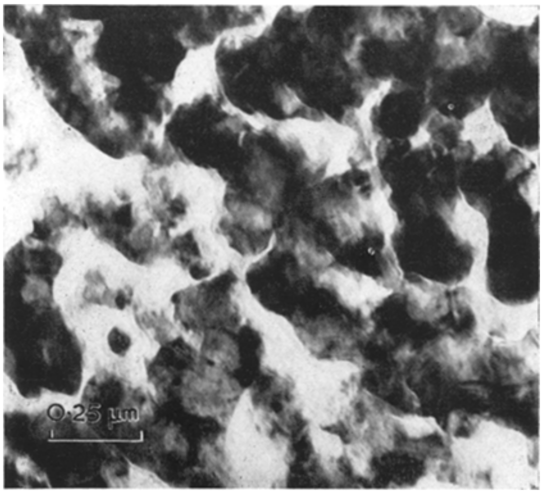

Figure 2 Micrograph of film of thickness 200 Å, coercivity 526 Oe, and pH 7.7.

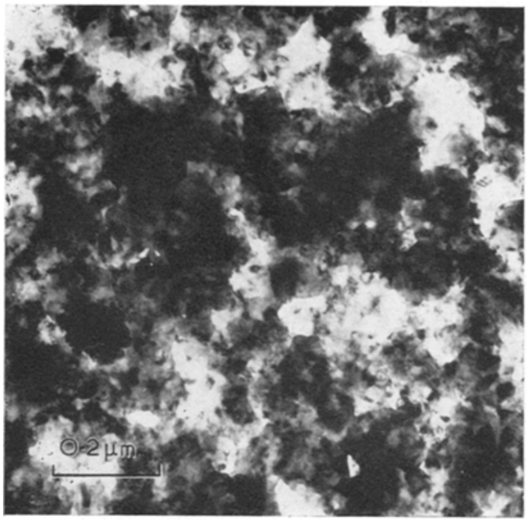

Figure 3 Micrograph (at 500 kV) of film of thickness 1000 Å, coercivity 270 Oe, and pH 7.4.

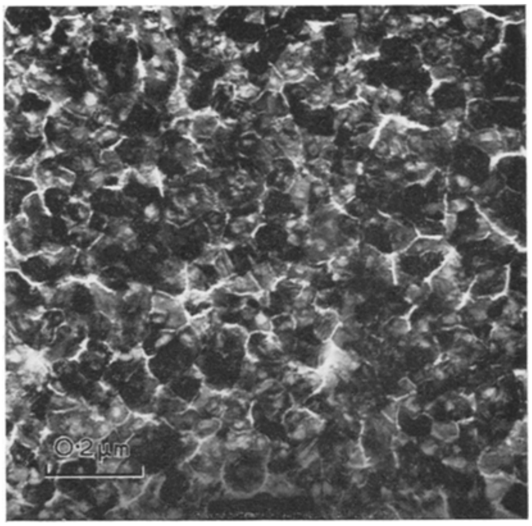

Figure 4 Micrograph of film of thickness 500 Å, coercivity 400 Oe, and pH 8.

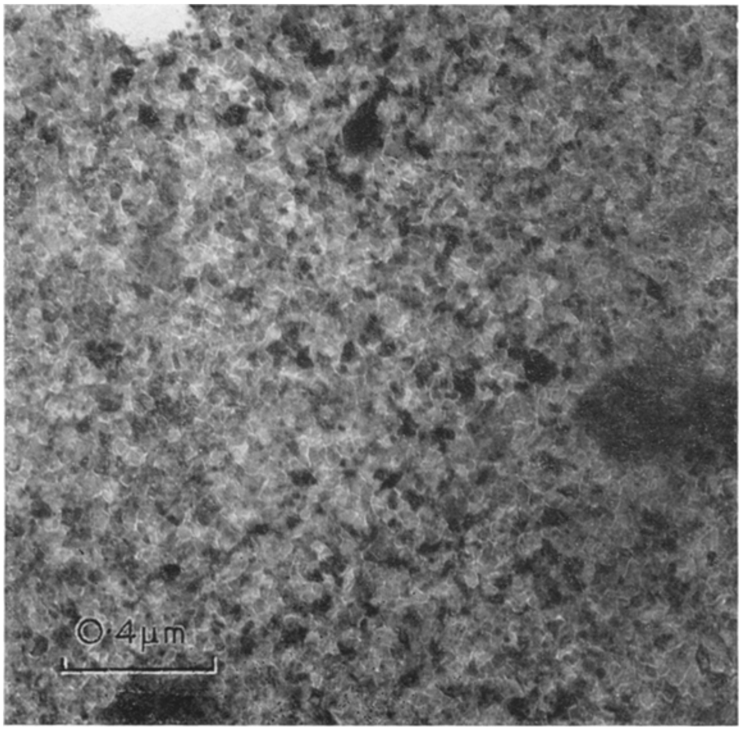

Figure 5 Micrograph (at 500 kV) of film of thickness 900 Å, coercivity 600 Oe, and pH 8.4.

especially the existence of groups of fringes which sometimes extended across a whole grain. Dark-field micrographs proved that these fringes were definitely caused by diffraction contrast, and were not merely artefacts. In many areas the fringes showed a high degree of regularity and were probably due to stacking faults: in other cases they were of the type associated with thickness variations. Using replica techniques Sallo and Olsen [6] also concluded that Co/P films were heavily faulted with individual grains consisting of a series of platelets.

We conclude this brief survey with a micrograph in fig. 5 of a higher pH value film, the limit of the workable range being about 8.5. Here, the presence of the channels was very pronounced and they even tended to a geometrical pattern in order to reduce grain-boundary energy. Possibly, as suggested by Fisher [7] in work on Co/P/Zn films, the channels owed their existence to the presence of phosphorus which is insoluble in cobalt, and would therefore have been expelled to the grain-boundaries. However, if the channels consisted entirely of phosphorus, it must have had a density less than the bulk value considering the small quantities (3% by weight) present in the plated film.

3.2. Annealing

Several samples were annealed in the electron microscope to examine their behaviour with heat-treatment, especially with regard to possible changes at the grain-boundaries. However, nothing significant was observed until 450° C, when the crystallite size rapidly increased, thus completely altering the aspect of the film. Simultaneously, the diffraction rings became sharper, as well as new ones arising from an fcc phase and oxides. Fig. 6 is typical of an annealed specimen (the same as fig. 5). Unfortunately, we were not able to measure the magnetic properties of samples heat-treated in this way, and a search for domain walls with Lorentz microscopy proved fruitless.

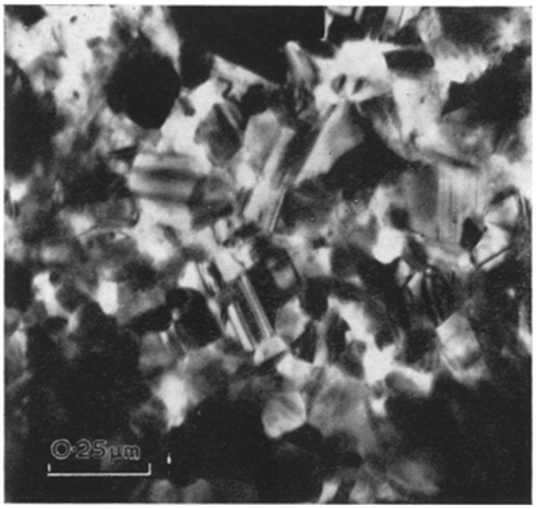

Figure 6 Micrograph of a film annealed at 450° C (the same specimen as shown in fig. 5).

3.3. Correlation with Magnetic Properties

There were two main structural tendencies observed with increasing pH value, namely the isolation of crystallites by channels of, presumably, a non-magnetic substance, and second, a greater continuity for a given thickness. The isolation of the particles is important in explaining the high coercivities of electroless films, since exchange interaction will be eliminated and magnetostatic interaction reduced. It is significant to note that, in general, the higher the pH, the higher the coercivity. The non-continuity of lower pH value films should also contribute to smaller coercivities since the clumps of crystallites may well be superparamagnetic. The factor of continuity may also influence the measured squareness ratio. We have examined pairs of samples of very thin films (200 Å) prepared under as similar conditions as possible but which showed a discrepancy in squareness. Microscopically the only observed difference was one of continuity, those with a low squareness consisting of clumps (see fig. 2) and thus making magnetostatic interaction difficult.

Finally, an important relation that could be obtained for those films where the grains were physically distinguishable was the variation of coercivity with crystallite size. Fig. 7 shows, as expected, an increase in coercivity with decreasing sizes of crystallites.

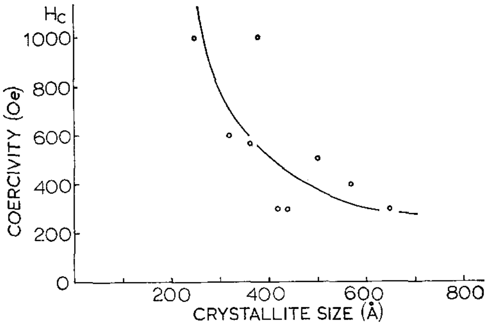

Figure 7 Variation of coercivity with crystallite size.

Acknowledgements

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