Effect of NH_4Cl on Microstructure and Magnetic Properties of Electrodeposited Co(P) Alloy

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In recent years, demand for the micro patterned ferromagnetic alloy has increased drastically for its soft and hard magnetic properties with applications in MRAM(magnetic random access memory), ultrahigh perpendicular recording media and MEMS(micro electro mechanical system) which is essential to fabricate microsystems like actuators and valves. Electrodeposition of ferromagnetic alloys has drawn much attention as an effective method for the fabrication of such micro devices mainly due to its ability to fill up patterns of high aspect ratio and to tailor the microstructure and properties as compared with the conventional vacuum deposition techniques such as CVD and PVD [1,2]. The objective of this study is to establish the electrodeposition process of a hard magnetic alloy to be incorporated as a part of the eye-implanted micro valve through which inner pressure of the eyeball is controlled to provide a cure for glaucoma. Cobalt/phosphorus alloy was chosen for superior hard magnetic properties and formation of thin films by electrodeposition is easily applicable [3-5]. In most cases, however, electrodeposited CoP was amorphous due to excessive phosphorus contents. Furthermore, fundamental studies on the electrochemical factors that can control the magnetic properties of hard magnetic alloy films are scarce, limiting their potential applications in many fields. It is therefore essential to elucidate the role of electrochemical factors controlling the magnetic properties such as coercivity and squareness to be tailored for specific applications or devices.

One of the most important additives in an electroplating bath is ammonium chloride functioning as a supporting electrolyte and pH buffer. Various effects of NH_4Cl addition are reported in the literature [6-8] and can be summarized as follows. Barcelo et al. [6] reported that the plating bath with high concentration of ammonium chloride improved the uniformity of the electrode surface. Baugh [7] paid attention to the role of ammonium chloride addition that removed oxygen atom or oxide layer on the electrode surface. Recently, Marozzi et al. [8] studied the effect of ammonium chloride and insisted that the presence of ammonium ion in an acidic solution markedly improved the mechanical properties of nickel elecrtodeposits. They suggested that if the concentration of NH_4Cl in the solution increased, attainable current density went up, thus mechanical property and adhesion of nickel electrodeposit on the substrate was improved. If pH becomes higher than 6, most metals such as nickel, zinc, cobalt are not electrodeposited as metallic phases [9]. Local pH at the electrode surface may become high by the electrode reaction, and unwanted hydroxide can be deposited. It is reported that ammonium chloride prevented this local pH at the electrode surface from increasing [10]. Ji et al. [10] was able to measure the pH locally and found that ammonium chloride is very effective to suppress the pH increase on the electrode surface thus acting as a buffering agent.

Results from this study indicates that the concentration of ammonium chloride is responsible for the variation of magnetic properties in CoP films while phosphorus content is kept constant. This implies that the coercivity variation of CoP with respect to NH_4Cl concentration is not due to compositional change of the CoP alloy and should be interpreted as the role of ammonium chloride affecting the electrodeposition mechanism, microstructure and/or crystallographic growth mechanism of CoP alloy. Therefore, the effect of ammonium chloride on CoP electrodeposition mechanism was studied with electroanalytical method such as cyclic voltammetry (**Fig. 1**) and microstructural characterization was conducted by employing XRD and TEM (**Fig. 2**) to correlate magnetic properties of electrodeposited CoP films with their crystallographic and microstructural features.

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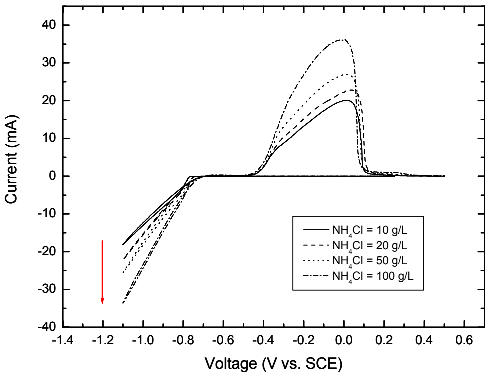

Fig. 1. The cyclic voltammograms measured in the solutions containing 10, 20, 50 and 100 g/l NH_4Cl, respectively.

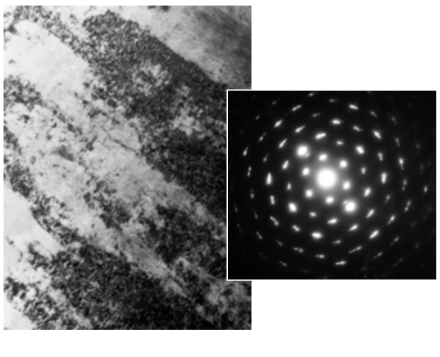

Fig. 2. Cross-sectional TEM image and diffraction pattern of CoP electrodeposited in the solution containing 100 g/l NH_4Cl.