Preparation and Characterization of Electrodeposited Co–Pt Binary Alloy Film^{*1}

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Co–Pt alloy films were electrodeposited from a novel bath which was designed in the present study containing the ammonia solution and ammonium tartrate as complexing agents. The Co–Pt deposited films were prepared with wide alloy compositions ranging from 16.5 at% Pt to 56.8 at% Pt by changing the bath concentration and current density. The structures of these deposited films were analyzed by means of XRD and HRTEM. The results indicated that the crystallographic structure of Co–Pt deposited film are the ϵ -Co solid solution when the platinum content in deposited film is below 31.1 at%, the mixture of ϵ -Co solid solution and (α -Co, Pt) face centered-cubic solid solution when the platinum in the deposited film is ranging from 35.7 at% to 45.7 at%, and the (α -Co, Pt) face centered-cubic solid solution when the platinum in the deposited film is ranging from 51.1 at% to 56.8 at%. Moreover, the ordered fct phase ($L1_0$) was detected with the help of XRD from Co–Pt deposited film with 51.1 at% Pt which was annealed in vacuum with pressure no lower 10^{-5} Pa for 60 min at the temperature of 450°C.

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1. Introduction

Co–Pt alloys have attracted significant attention as possible ultra-high-density recording media because of their uniaxial magnetocrystalline anisotropy [$K_u \cong 4.9 \times 10^7$ erg/cm³],¹⁾ high coercive force and good chemical stabilities. These characteristics have prompted numerous studies of the properties of Co–Pt, both in bulk and in thin film form.^{2,3)}

According to the thermal equilibrium phase diagram of Co–Pt binary alloy system⁴⁾ (Fig. 1(a)), two super-lattices, CoPt and CoPt₃ form at low temperature state. The CoPt has one ordered face-centered tetragonal $L1_0$ type of structure,

and then has the effect of greatly increasing the coercivity over that of the disordered alloy. Until now, the preparation of the Co–Pt alloy film has mainly relied on the sputtering method and vacuum deposition technique.^{5,6)} However, the preparation of Co–Pt alloy film by using electrodeposition method has not yet been clearly since the preparation of stable and effective deposition electrolyte is very difficult.^{7,8)}

The intent of the present study was to design the novel bath and efficient deposition condition for preparing the Co–Pt alloy film with a wide range alloy composition by using the electrodeposition method. The crystallographic structure of deposited film has been studied by using XRD and HRTEM. Finally, the annealed deposited film with CoPt ordered fct structure has also determined with the help of XRD.

2. Experimental Procedure

The Co–Pt deposited films were obtained from the solutions containing $H_2PtCl_6 \cdot 6H_2O$ (0.05- x mol/L), $CoCl_2 \cdot 6H_2O$ (x mol/L), and $(NH_4)_2C_4H_4O_6$ (2 x mol/L) as the complex-forming agent adjusted in pH to 9.5 with the aid of $NH_3 \cdot H_2O$. Current density was controlled from 100 to 2000 A/m², and the bath temperature was maintained at 60°C. The Co–Pt alloy film was deposited on copper foil with the thickness of 0.035 mm, which was electrochemically polished to a mirror finish surface. The anode was a platinum film coated on the titanium mesh.

The chemical composition of the Co–Pt alloy was measured by the energy dispersive X-ray spectrometry (EDS) (JED-2001, JEOL). The structure of the deposited film was determined by X-ray diffraction (XRD) (M21X TXJ-FO88, MAC Science) and a high-resolution transmission electron microscope (HRTEM) (JEM-2010F, JEOL). To characterize the structural variations with temperature by X-ray diffraction, the sample was annealed in vacuum with pressure no lower 10^{-5} Pa for 60 min at the temperature of 450°C.

Fig. 1 Thermal equilibrium phase diagram of Co–Pt binary alloy system⁴⁾(a), phase diagram of Co–Pt deposited film obtained in the present study (b).

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Fig. 2 Relationship between Pt content in deposited film and Pt ion concentration in bath under various current density (a) 400 A/m², (b) 600 A/m², (c) 800 A/m², (d) 1500 A/m².

3. Results and Discussion

3.1 Chemical composition of deposition films

The standard reduction potentials of cobalt and platinum are -0.287 V and 1.19 V, respectively. In order to bring the potentials of cobalt and platinum close enough so that co-deposition can be carried out, the ammonia solution and ammonium tartrate were used to form complexing with metallic ions in aqueous solution.

Figure 2 shows the relationship between platinum content in deposited films and platinum concentration in bath under various current densities. It can be found that the platinum content in the deposited film increases with increasing the platinum ions concentration in the bath. However, the platinum content in the deposited film is always lower than Pt ions concentration in the bath, since Pt at% in the deposited films lies below its composition reference line (dotted line in Fig. 2). These results imply that platinum is not readily deposited comparing with cobalt in aqueous solution and therefore the Co–Pt deposition can be defined as “anomalous co-deposition”.⁹⁾ Moreover, the Pt content increases with increasing the cathodic current density.

Based the above result, it can be concluded that the Co–Pt alloy films with the alloy composition ranging from 16.5 at% Pt to 56.8 at% Pt have been electrodeposited from the bath using the $\text{NH}_3\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ as complex-forming additives.

3.2 X-ray diffraction characterization

X-ray diffraction studies were carried out to analyze various Co–Pt deposited films at different platinum content. According to the diffraction patterns shown in Fig. 3, in the range of 16.5–31.1 at% Pt, two sharp peaks appear around $2\theta = 40.0^\circ$, 45.8° . These two peaks are almost similar to the standard diffraction peak of ϵ -cobalt with hexagonal close packed lattice, but shifted to the low degree side, which can be attributed to the ϵ -Co solid solution. When the platinum content in the deposited film reaches 35.7 at%, one sharp peak at $2\theta = 41.9^\circ$ and the other relatively broad peak at $2\theta = 48.5^\circ$ appear as a second phase while ϵ -Co phase

Fig. 3 X-ray diffraction patterns of the deposited films at different Pt content (a) 16.5 at% Pt, (b) 25.1 at% Pt, (c) 31.1 at% Pt, (d) 35.7 at% Pt, (e) 41.4 at% Pt, (f) 45.6 at% Pt, (g) 51.1 at% Pt, (h) 56.8 at% Pt.

completely disappears when the platinum content in the deposited film reaches up to 51.1 at%. The peaks at $2\theta = 41.9^\circ$ and 48.5° are almost similar to the standard diffraction peak of platinum or that of α -cobalt with face-centered cubic lattice, but shifts to the low degree side, which can be attributed to the (α -Co, Pt) face centered-cubic solid solution. The fcc solid solution maintains until the platinum content in the deposited film reaches 56.8 at%.

The relationship between the crystallographic structure and alloy composition of deposited film can be displaced in Fig. 1(b). The Co–Pt deposited film exists as the ϵ -Co solid solution when the platinum content in the deposited film is below 31.1 at%, the mixture of ϵ -Co solid solution and (α -Co, Pt) face centered-cubic solid solution when the platinum in the deposited film is ranging from 35.7 at% to 45.6 at%, and the (α -Co, Pt) face centered-cubic solid solution when the platinum in the deposited film is ranging from 51.1 at% to 56.8 at%.

From the XRD results (Fig. 3), the variations of the lattice constant of (α -Co, Pt) face-centered cubic solid solution were calculated based on the diffraction line (111). As shown from Fig. 4, it is found that the lattice constant increases linearly with increasing the Pt content in the deposited film, being in good agreement with the Vegard's law. However, the Co–Pt alloys are predicted to form the CoPt, CoPt₃ and their mixtures at the lower temperature state from the thermal equilibrium phase diagram (Fig. 1(a)). These results indicated that the Co–Pt deposited film forms a different phase than the stable phase predicted by the thermal equilibrium phase diagram at room temperature, which is a meta-stable phase.

The lattice constant of ϵ -Co solid solution was calculated with diffraction line of (100), and the trend of lattice constant of α -Co solid solution along with the increase of platinum content in the deposited film is shown in Fig. 5. The lattice constant increases with increasing the platinum content in the deposited film, showing a super-saturated solid solution structure in Co–Pt deposited film.

Fig. 4 The variation of the lattice constant of (α -Co, Pt) fcc solid solution.

Fig. 5 The variation of the lattice constant of ϵ -Co solid solution.

3.3 HRTEM observations

HRTEM observations were also carried out to confirm the results obtained from XRD. Figure 6 shows HRTEM micrographs of the Co–Pt deposited films at different platinum content with bright field images and electron diffraction patterns. It is found that all the deposited films show the fine-grained structures and the crystal size changes with changing the Pt content in the deposited film. The crystal size of the

deposited film with 51.1 at% Pt which was measured based on the lattice image, is estimated to be about 5.0 nm, showing the most finest crystal structure in the deposited films. This result is also in accordance with that obtained from the X-ray diffraction pattern, which was calculated by using Scherrer's formula.

Moreover, as shown in the electron diffraction patterns of the deposited films, the film with 16.5 at% Pt (Fig. 6(a))

Fig. 6 Lattice images and electron diffraction patterns of Co–Pt deposited films (a) 16.5 at% Pt, (b) 37.2 at% Pt, (c) 41.4 at% Pt, (d) 51.1 at% Pt, (e) 56.8 at% Pt.

shows a single ε -Co phase with hexagonal close packed lattice. However, as shown in Fig. 6(b) to (e), the structures of deposited films change from ε -Co phase to the (α -Co, Pt) face-centered cubic solid solution with increasing the platinum content in the deposited film. It can be found that HRTEM results are in accordance with the XRD results (Fig. 3).

3.4 Influence of annealing on the crystallographic structure of deposited film with 51.1 at% Pt

As explained above, it has been clearly that the Co–Pt deposited film form a different phase than the stable phase predicted by the thermal equilibrium phase diagram, which is a meta-stable phase. Then it is expected that the structure of as-deposited film can be transformed into the equilibrium phase by annealing. In this case, the equilibrium phase is CoPt or CoPt₃ with so-called super-lattice structure.

For this intent, the deposited film with 51.1 at% Pt was chosen as the specimen and was annealed under vacuum with pressure no lower 10^{-5} Pa for 60 min at 450°C. Figure 7 shows variation of XRD pattern of the deposited film with 51.1 at% Pt by 60 min annealing. As-deposited film shows a chemically disordered fcc structure. Annealing induced the

Co and Pt atoms to rearrange into the long-range chemically ordered fct structure, as indicated by evolution of (001), (110) and other peaks. This is the evidence that the structure of deposited film with 51.1 at% Pt transforms into ordered fct structure by annealing.

4. Conclusions

The novel bath for electrodeposition of Co–Pt alloy film has been prepared successfully. By using the bath, the Co–Pt films with wide platinum content were electrodeposited by changing bath concentration and electrodeposition conditions. The results indicated that the crystallographic structure of Co–Pt deposited film is the ε -Co solid solution for the deposited film with platinum content ranging from 0 to 31.1 at%, the mixture of ε -Co solid solution and (α -Co, Pt) face centered-cubic solid solution for deposited film with platinum content ranging from 35.7 at% to 45.6 at%, and the (α -Co, Pt) face centered-cubic solid solution for deposited film with platinum content ranging from 51.1 at% to 56.8 at%. Moreover, the ordered fct structure ($L1_0$) occurs in the annealed Co–Pt alloy film with 51.1 at% Pt.

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REFERENCES

- 1) D. Weller, A. Moser, L. Folks, M. E. Best, W. Lee, M. F. Toney, M. Schwickert, J.-U. Thiele and M. F. Doerner: IEEE. Trans. Magn. **36** (2000) 10–15.
- 2) S. H. Liou, Y. Liu, S. S. Malhotra, M. Yu and D. J. Sellmyer: J. Appl. Phys. **79** (1996) 5060–5062.
- 3) D. M. Artymowicz, B. M. Lairson and B. M. Clemens: J. Cryst. Growth **169** (1996) 83–88.
- 4) N. Nagasaki, M. Hirabayashi: *Thermal Equilibrium Phase Diagrams of Alloy*, (Agune Technology Center, Tokyo, 2001) pp. 112.
- 5) R. A. Ristau, K. Barmak, L. H. Lewis, K. R. Coffey and J. K. Howard: J. Appl. Phys. **86** (1999) 4527–4533.
- 6) C. Chen, O. Kitakami, S. Okamoto and Y. Shimada: IEEE. Trans. Magn. **35** (1999) 3466–3468.
- 7) Y. Jyoko and W. Schwarzacher: Electrochem. Solid-State Lett. **3** (2000) 377–380.
- 8) L. Callegaro, E. Puppini, P. L. Cavallotti and G. Zangari: J. Magn. Mater. **155** (1996) 190–192.
- 9) A. Brenner: *Electrodeposition of alloys*, (ACADEMIC PRESS, New York and London, 1963) pp. 84–87.

Fig. 7 Variation of X-ray diffraction patterns of Co–Pt deposited film with 51.1 at% Pt annealed under vacuum with pressure no lower 10^{-5} Pa for 60 min at 450°C, (a) as-deposited film, (b) annealed film.