Amorphous Co–Ni–P Alloys with High Saturation Magnetization Produced by Electrodeposition

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The composition, structure and magnetic properties of high cobalt-containing Co–Ni–P alloys have been examined by controlling electrodeposition parameters. The alloys were deposited at 323 K from an electroplating solution consisting of nickel and cobalt chlorides and sodium hypophosphite. The current density and pH of the solution were controlled to determine the conditions of forming amorphous films. The alloys prepared at a current density of 150 A/m² and pH of 5.20 include both amorphous and crystalline phases. The increase of pH to above 5.20 results in the formation of amorphous alloys without crystalline phase. The conditions of 220 A/m² for current density and 5.24 for pH were optimum to prepare the amorphous alloy at the highest deposition rate of 5.19×10^{-5} kg/m²/s. These amorphous alloys exhibited high saturation magnetization up to 1.3 T with coercivity of about 20 kA/m.

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1. Introduction

Studies on metallic amorphous alloys and their functional properties have been an important subject for scientists and researchers during the last two decades. This has been attributed to novel mechanical,^{1–4)} magnetic^{5–8)} and catalytic^{9–11)} properties and excellent corrosion resistance^{12–17)} for these materials. Among magnetic amorphous materials, Co-based alloys are important and have been produced by various techniques including rapid quenching,^{18,19)} physical vapor deposition,²⁰⁾ chemical or electroless plating^{21,22)} and electrodeposition.^{23–29)} The alloys produced by electrodeposition include Co–P, Co–W and Co–Ni–P *etc.* It is known that these Co-based magnetic alloys have relatively low saturation magnetization values below 1.0 T. Recently, Myung *et al.*³⁰⁾ have produced Co–Ni–P crystalline alloys having high cobalt and low phosphorus contents. It has been characterized that these alloys exhibit rather high saturation magnetization in the range of 1.2 to 1.4 T. In this work, we examine optimum conditions for the formation of amorphous alloys with relatively high saturation magnetization values up to about 1.2 T from a similar electroplating solution.

2. Experimental

The composition of the electroplating bath is shown in Table 1. It consists of cobalt and nickel chlorides as a source of Co and Ni ions, respectively, and sodium hypophosphite as a source of phosphorus. Boric acid was added as a bath stabilizer. Sodium chloride was added to improve the conductivity of the solution, while sodium saccharin was added to improve the quality of the deposit. pH of the solution was controlled by sodium citrate. It also acts as a complexing agent for cobalt ions and maintains the cobalt contents of the alloys at higher percentages. pH remained constant during the deposition. Fresh solution was used for each deposition.

Copper plates of 3.25×10^{-4} m² in surface area were used

Table 1 Composition and operating conditions for the electroplating bath.

Basic bath composition	
NiCl ₂ ·6H ₂ O	0.2 mol/L
CoCl ₂ ·6H ₂ O	0.15 mol/L
NaH ₂ PO ₂ ·H ₂ O	0.3 mol/L
H ₃ BO ₃	0.4 mol/L
NaCl	0.7 mol/L
C ₇ H ₄ NNaO ₃ S	0.03 mol/L
Operating conditions	
Temperature	323 K
Time	1.8 ks
pH	4.04–5.37
Current density	50–220 A/m ²

as substrates and cobalt plate as anode or counter electrode. Before electroplating, the copper plates were mechanically polished on SiC papers up to 2000 grit and washed in an alkaline solution. Then, they were chemically polished in an acidic solution, dried and used for electroplating. Potential on the substrate surface was measured against saturated calomel electrode (SCE). The constant current was applied by using a Hokuto Denko HZ-3000 electrochemical measuring system. The temperature of the bath was maintained at 323 K by a thermostat. The weight of the substrate was measured before (W_1) and after (W_2) the plating and the difference (ΔW) was taken as the weight of the deposited alloy, which was used for the calculation of magnetic induction values.

The crystalline and amorphous structures were determined by XRD. The thermal stability of the deposited alloys was determined by DSC using SII-320 DSC system. The amorphicity was also examined by transmission electron microscopy (TEM). The chemical composition was determined with a scanning electron microscope (SEM, Hitachi S-800) equipped with Kevex energy dispersive spectroscopy (EDS) system. Magnetic hysteresis loops (applied field vs. magnetic induction) for the deposited alloys were measured with a vibrating sample magnetometer (VSM). Since the specimens for magnetic measurements consisted of Co–Ni–P

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alloy films deposited on copper substrate, their magnetic properties included the contribution from the copper substrate. This contribution was corrected by measuring the hysteresis loop for unplated copper substrate under similar conditions and subtracting the later value from the former one.

3. Results

Figure 1 shows the effect of current density on the composition of the alloys electroplated at a pH of 4.04. In this case, no sodium citrate was added to the bath. It is observed that the cobalt content of the alloy is about 14 at% at a current density of 50 A/m² and increases rapidly to 73 at% with an increase of current density to 90 A/m². At the same time, phosphorus content decreases from 5.2 to 2.0 at%. However, the composition remains approximately constant in the range from 90 to 150 A/m². With further increasing current density to above 150 A/m², the cobalt content again decreases and the phosphorus content increases. The alloys deposited in the range of 90 to 150 A/m² are of interest because of high cobalt and low phosphorus contents. Such alloys are expected to exhibit better soft magnetic properties.

Fig. 1 Effect of current density on the composition of electrodeposited alloys at pH of 4.04.

It is recognized that the structure becomes finer in this specific range of current density. Figure 2 shows SEM images of the surface of the alloys deposited in the specific range, together with that of the alloy deposited at 50 A/m².

Fig. 2 Surface features of alloys deposited at pH of 4.04 and current density of (a) 50 A/m², (b) 90 A/m², (c) 110 A/m² and (d) 150 A/m².

The micrograph (d) is shown at higher magnification because it has smoother surface structure invisible at lower magnification. It is clearly visible from these micrographs that the surface becomes finer with increasing current density. The surface ruggedness of the alloy deposited at 150 A/m^2 is of the order of 250 nm .

Figure 3 shows X-ray diffraction patterns of the above-mentioned alloys. The alloys prepared at current densities of 50 and 70 A/m^2 show nickel peaks, while those deposited from 90 to 150 A/m^2 show cobalt peaks. However, the cobalt alloys are highly textured along (002) plane of hexagonal phase. The alloys deposited at 50 and 70 A/m^2 also show nickel phosphide peaks, while those deposited at 90 to 150 A/m^2 show cobalt phosphide peaks.

Since the finest structure for the high cobalt-containing alloys was obtained at 150 A/m^2 , the effect of pH was studied at this current density. Figure 4 shows the effect of pH on the composition of the alloys deposited at a current density of 150 A/m^2 . The pH was changed by the addition of sodium citrate in the solution. Sodium citrate also acts as a complexing agent for cobalt and thus in the electrodeposited alloys maintains high cobalt contents at higher pH values. It is evident from Fig. 4 that up to the pH of 5.15 , the cobalt content of the deposited alloys is in the range of 74 to $78 \text{ at}\%$, while the phosphorus content increases from $1.76 \text{ at}\%$ at 4.04 pH to $4.3 \text{ at}\%$ at 5.15 pH . With an increase of phosphorus content, it is seen that the structure texture changes from (002) plane to (100) plane as shown in Fig. 5. When the pH of the plating solution increases to 5.20 , the phosphorus

Fig. 3 X-ray diffraction patterns for alloys deposited at pH of 4.04 and different current densities.

Fig. 4 Effect of pH on the composition of electrodeposited alloys at current density of 150 A/m^2 .

Fig. 5 X-ray diffraction patterns for alloys deposited at current density of 150 A/m^2 and different pH values.

content increases to $6.3 \text{ at}\%$ and an amorphous phase appears in the deposited alloy. In this case, the cobalt content also decreases to $68 \text{ at}\%$. With a further increase in pH, the phosphorus content does not change and remains approximately constant ($6 \text{ at}\%$). However, the cobalt content increases and the structure becomes completely amorphous as far as determined by XRD.

Figure 6 shows the effect of pH on the deposition rate of the alloys. The deposition rate decreases with an increase in pH. It is evident that the pH value for the formation of films

Fig. 6 Effect of pH on the deposition rate of alloys electrodeposited at current density of 150 A/m^2 .

with a completely amorphous structure at the highest deposition rate is 5.24. Therefore, the effect of current density was studied at a constant pH of 5.24.

Figure 7 shows the effect of current density on the composition of the deposited alloys at the pH of 5.24. It is seen that the composition is not affected much by current density and the cobalt content in the alloys is in the range of 74 to 78 at%, while the phosphorus content lies in the range of 5 to 6 at%. However, the quality of the films formed at current densities higher than 220 A/m² was not good and they contained entrapped salt. It is seen in Fig. 8 that the deposition rate increases with increasing current density. However, the use of current densities higher than 220 A/m² is not advisable because of salt entrapment.

Figure 9 shows the electron diffraction pattern of the alloy deposited at a current density of 220 A/m² and a pH of 5.24. The diffraction pattern reveals typical halos due to the formation of an amorphous phase. Figure 10 shows the DSC curve of the same alloy. The curve shows two crystallization peaks. The onset point lies at 514 K for the first peak and at 683 K for the second peak. These results also show that this alloy has an amorphous structure.

Figure 11 shows the changes in the saturation magnetization (I_s) and remanence (I_r) with pH for the amorphous alloys deposited at a current density of 150 A/m². The saturation

Fig. 9 TEM diffraction pattern of the alloy deposited at current density of 220 A/m² and pH of 5.24.

Fig. 7 Effect of current density on the composition of alloys electro-deposited at pH of 5.24.

Fig. 10 DSC curve of the alloy deposited at current density of 220 A/m² and pH of 5.24.

Fig. 8 Effect of current density on the deposition rate of alloys electro-deposited at a pH of 5.24.

Fig. 11 Effect of pH on the saturation magnetization (I_s) and remanence (I_r) of alloys electrodeposited at current density of 150 A/m².

magnetization is 1.30 T for the alloy containing crystalline phase deposited at pH of 5.20 and decreases from 1.20 T at pH = 5.24 to 1.16 T at pH = 5.37 for the alloys containing only an amorphous phase. The remanence also decreases with increasing pH of the solution.

The coercivities of these alloys are shown in Fig. 12. These alloys show larger coercivities and cannot be regarded as a soft magnetic material. The reason for the larger coercivities for these amorphous alloys is not clear at present.

Figure 13 shows the saturation magnetization and remanence values for the alloys deposited at pH of 5.24 and various current densities. It is seen that the increase of the current density also causes a decrease in saturation magnetization and remanence. With an increase in current density from 150 to 220 A/m², the saturation magnetization drops from 1.20 to 1.06 T. The effect of current density on coercivity is also similar to that of pH. The coercivity decreases with an increase in the current density. Figure 14 shows that an increase of current density from 150 to 220 A/m² causes a decrease in coercivity from 21.2 to 18.3 kA/m. The magnetic properties of the alloy deposited under the conditions of 220 A/m² and 5.24 pH are also shown in Fig. 15. It is clearly evidenced from the hysteresis loop that this alloy has saturation magnetization of 1.06 T, remanence of 0.26 T and coercivity of 18.3 kA/m.

Fig. 12 Effect of pH on the coercivity of alloys electrodeposited at current density of 150 A/m².

Fig. 13 Effect of current density on the saturation magnetization (I_s) and remanence (I_r) of alloys electrodeposited at pH of 5.24.

Fig. 14 Effect of current density on the coercivity of alloys electrodeposited at pH of 5.24.

Fig. 15 Magnetic hysteresis loop for the alloy electrodeposited at current density of 220 A/m² and pH of 5.24.

4. Discussion

4.1 Current density and composition

It is known that current density has a strong effect on the composition of electrodeposited Co–Ni–P alloys. However, the behavior of composition vs. current density curves shown in Figs. 1 and 7 is different. Although the behavior in Fig. 1, at low and high current densities, can be explained on the basis of thermodynamics and kinetics of the process, it is difficult to explain the behavior in the current density range of 90 to 150 A/m². Since the deposition potential for nickel is lower than that for cobalt, nickel is deposited preferentially at lower overpotentials associated with lower current densities. As the current density is increased, the cobalt concentration in the deposited alloys increases. Such a behavior is common for these alloys. On the other hand, the increase in the nickel content at the current densities higher than 150 A/m² is associated with the kinetics of the process. At such high current densities, the cobalt ions are consumed very fast. As a result, the cobalt ions are depleted in the vicinity of the electrode and this causes preferential deposition of nickel. When both ions are depleted in the vicinity of the electrode, the deposition is dependent only on the diffusion of ions from bulk solution to the electrode surface. Under such conditions, approximately equal amounts of the two elements should be deposited due to relatively comparable diffusion coefficients.

It is evidenced from Fig. 1. However, the reason for the constant composition with increasing current density from 90 to 150 A/m² at pH of 4.04 remains unclear. Similarly, no prominent effect of current density is recognized on the composition of the alloys deposited at pH of 5.24. In this case sodium citrate seems to play an important role, acting as a complexing agent for cobalt ions, in controlling the kinetics of the deposition process. It must be noted that cobalt ions do not deplete from the solution overall, as cobalt is used for anode.

4.2 Saturation magnetization and coercivity

As shown in Figs. 11 to 15, the present Co–Ni–P amorphous alloys exhibit high saturation magnetization and coercivity than conventional amorphous Co–Ni–P alloys. The high saturation magnetization may be attributed to lower phosphorus contents of the alloys. The previously reported Co–Ni–P amorphous alloys have phosphorus contents more than about 10 at%, while the present alloys have phosphorus content of 6 at% or less than 6%. It is known²⁹ that Co–P binary amorphous alloys have higher coercivity when the phosphorus content is less than 9 at%. The coercivity decreases drastically as the phosphorus content increases to above 9 at%. There has been no detailed study on the reason for high coercivity of these Co–P alloys. The Co–Ni–P alloys produced in the present work also exhibit high coercivity, but the reasons for the high saturation magnetization and coercivity for these alloy films remain unclear. To find out the influence of phosphorus content on the coercivity of these alloys, particularly, an optimum phosphorus content at which these amorphous alloys exhibit good soft magnetic properties is under investigation.

5. Conclusions

At pH of 4.04, the composition of the Co–Ni–P alloys was found to be independent of current density in the current density range of 90 to 150 A/m². By controlling the pH in this range high Co- and low P-containing amorphous alloys were prepared. The deposition rate of these amorphous alloys decreases with increasing pH of the bath, and increases with increasing current density. The alloy produced at a current density of 220 A/m² and a pH of 5.24 has the highest deposition rate. These amorphous alloys exhibited high saturation magnetizations of 1.06 to 1.2 T and relatively large coercivities of about 20 kA/m.

REFERENCES

- 1) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: *Acta Mater.* **49** (2001) 2645–2652.
- 2) Y. Kawamura, K. Hayashi, J. Koike, A. Kato, A. Inoue and T. Masumoto: *Mater. Sci. Forum* **350** (2000) 111–116.
- 3) A. Inoue and H. Kimura: *Mater. Sci. Eng. A-Struct.* **286** (2000) 1–10.
- 4) A. Inoue, T. Zhang and Y. H. Kim: *Mater. Trans., JIM* **38** (1997) 749–755.
- 5) A. Inoue, T. Zhang and A. Takeuchi: *Appl. Phys. Lett.* **71** (1997) 464–466.
- 6) A. Inoue and B. L. Shen: *Mater. Trans.* **43** (2002) 2350–2353.
- 7) D. H. Shin, H. Niedoba, Y. Henry, F. Machizaud, V. Brien, D. Chumakov, R. Schafer and G. Suran: *J. Magn. Magn. Mater.* **249** (2002) 422–427.
- 8) J. Diaz, N. Hamdan, P. Jalil, Z. Hussain, S. M. Valvidares and J. M. Alameda: *IEEE Trans. Magn.* **38** (2002) 2811–2813 (Part 1).
- 9) Z. L. Ma, R. L. Jia, C. J. Liu and Z. T. Mi: *Chem. Lett.* **9** (2002) 884–885.
- 10) M. Janik-Czachor, A. Szummer, J. Bukowska, A. Molnar, P. Mack, S. M. Filipek, P. Kedzierzawski, A. Kudelski, M. Pisarek, M. Dolata and M. Varga: *Appl. Catal. A-Gen.* **235** (2002) 157–170.
- 11) Y. Lu, Z. T. Xiong, J. T. Li and J. Y. Lin: *Catal. Lett.* **78** (2002) 231–237.
- 12) M. Mehmood, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: *Corros. Sci.* **42** (2000) 361–382.
- 13) A. A. El-Moneim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: *Mater. Sci. Eng. A-Struct.* **267** (1999) 285–293.
- 14) M. Mehmood, B. P. Zhang, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto: *Corros. Sci.* **40** (1998) 1–17.
- 15) H. Habazaki, T. Sato, A. Kawashima, K. Asami and K. Hashimoto: *Mater. Sci. Eng. A-Struct.* **304** (2001) 696–700 (Sp. Iss. SI).
- 16) V. Cremaschi, I. Avram, T. Perez and H. Sirkin: *Scr. Mater.* **46** (2002) 95–100.
- 17) C. A. C. Souza, J. E. May, I. A. Carlos, M. F. de Oliveira, S. E. Kuri and C. S. Kiminami: *J. Non-Cryst. Solids* **304** (2002) 210–216.
- 18) A. Inoue and B. L. Shen: *Mater. Trans.* **43** (2002) 1230–1234 (Sp. Iss. SI).
- 19) W. Zhang, Y. Long, M. Imafuku and A. Inoue: *Mater. Trans.* **43** (2002) 1974–1978.
- 20) J. M. Fallon, C. A. Faunce and P. J. Grundy: *J. Phys.-Condens. Mat.* **12** (2000) 4075–4089.
- 21) S. Ya. Kiparisov and V. V. Vershinin: *The Physics of Metals and Metallography* **92** (2001) 25–30.
- 22) Yu. O. Akulova and N. O. Gonchukova: *Glass Physics and Chemistry* **24** (1998) 552–556.
- 23) J. M. Garcia, A. Asenjo, J. P. Sinnecker and M. Vazquez: *J. Magn. Magn. Mater.* **215** (2000) 352–354 (Sp. Iss. SI).
- 24) C. Favieres, M. C. Sanchez, E. Lopez, C. Aroca, P. Sanchez and V. Madurga: *J. Magn. Magn. Mater.* **177** (1998) 107–108 (Part 1).
- 25) G. Rivero, M. Multigner, J. M. Garcia, P. Crespo and A. Hernando: *J. Magn. Magn. Mater.* **177** (1998) 119–120 (Part 1).
- 26) A. Budniok and J. Kupka: *Electrochim. Acta* **34** (1989) 871–873.
- 27) A. Garcia-Arribas, M. L. Fdez-Gubieda and J. M. Barandiaran: *Phys. Rev. B* **61** (2000) 6238–6245.
- 28) M. M. V. Parente, O. R. Mattos, S. L. Diaz, P. L. Neto and F. J. F. Miranda: *J. Appl. Electrochem.* **31** (2001) 677–683.
- 29) A. Darkowski: *Surf. Coat. Tech.* **30** (1987) 131–135.
- 30) N. V. Myung, D. Y. Park, M. Schwartz, K. Nobe, H. Yang, C. K. Yang and J. W. Judy: 6th Int. Symp. on Magnetic Materials, Processes and Devices, *Proc. Electrochem. Soc. PV 2000-29* (2000).