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Research Article

Effects of High Magnetic Field Postannealing on Microstructure and Properties of Pulse Electrodeposited Co-Ni-P Films

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The influence of high magnetic field annealing on the morphology, microstructure, and properties of pulsed-electrodeposited Co-Ni-P films was investigated. The as-deposited film with a rough surface changed into uniform nanocrystalline during the magnetic field annealing process. In particular, the formation of intestine-like appearance with spherical clusters vanishing is favored from a moderate magnetic field strength of 6 T, due to the polarized effects. Meantime, the diffraction peak (111) of α (fcc) phase shifts to the right direction, which is attributed to the fact that more Co atoms from phosphide phase are incorporated into the Ni lattice, in comparison with the case of annealing under 0 T and 12 T magnetic fields. The mechanical and magnetic properties of the films reach relative optimum values at $B = 6$ T. The evolution of magneto-induced modification in the Co-Ni-P morphology, structure, and properties can be explained by the polarized effect and the diffusion-acceleration effect under a high magnetic field.

1. Introduction

Widespread interests were focused on Co-based alloys thin films because of their magnetic properties and their extensive technological application in microelectronics and automotive industries [1–3]. Most of earlier reports pointed out the soft magnetic properties of an electrodeposited Co-based alloy, such as Co-Ni-P alloy films, for data storage devices. Recently, there have been a number of investigations on the perpendicular magnetic anisotropy of Co-Ni-P films for high density recording. On the other side, Co-Ni-P alloy, with a special composition ratio, is a prospective hard magnetic material for microelectromechanical systems (MEMS) application [4, 5] and perpendicular magnetic recording media [6, 7], because of its relatively high magnetic saturation (M_s) and coercivity (H_c). Electrodeposition Co-Ni-P alloy films have many advantages over electroless deposition and vacuum processes: easy maintenance, low temperatures, and the ability to control microstructure and properties. In particular, because of the higher instantaneous current density in comparison to direct current plating, pulse-electrodeposition has been found to be an effective means of perturbing the adsorption/desorption processes and hence offers an opportunity of controlling the microstructure of the electrodeposits. In addition, the pulse-electrodeposition method attracts much attention as it significantly raises the limiting current density, eliminates thickness, and improves step coverage of thin films [8].

Plenty of research has been devoted to preparing of Co-Ni-P films with tunable microstructure and properties by pulse-electrodeposition method. Generally, the microstructure of electrodeposited thin films was controlled by adjustment of the deposition parameters, such as current density [9], pH value of the solution, and superimposed external magnetic field [10, 11] during the electrodeposition process. Moreover, the heat treatment method was also widely used to tune the microstructure and improve the thermal stability of CoNiP films. [12, 13]. Nowadays, research has suggested that magnetic field annealing is useful for tailoring the microstructure of the as-deposited nanocrystalline films [14, 15]. Li et al. [16] demonstrated that using magnetic field annealing around the Curie temperature can obtain preferential orientation (001) and perpendicular anisotropy in FePt films. Markou et al. [17] established that high degree (001) texture in $L1_0$ CoPt films can be obtained by annealing Co/Pt bilayers in a perpendicular magnetic field of 1 k Oe. Though there is an important role played by magnetic fields in the grain growth, diffusion, and recrystallization of the ferromagnetic film during annealing process, the required annealing temperatures are normally higher than the Curie point that limits the employment of magnetic annealing. Few applications of high magnetic field (over 10 T) during annealing process [18, 19] prove it to be a promising method to "tailor" the final microstructure (e.g., grain size, crystallographic orientation, and surface topography) and related properties of Co-Ni-P magnetic film.

In this work, the high magnetic fields with different strength were used to anneal the pulsed-electrodeposited Co-Ni-P films. The influences of high magnetic field annealing on the surface morphology, crystal structure, and related mechanical and magnetic properties were studied. The applied high magnetic field is expected to find a new strategy to tune the microstructure and properties of as-deposited thin films.

2. Experimental Procedure

Nanocrystalline Co-Ni-P films were pulse-electrodeposited on cathodes (1 cm^2) with structure of Cu substrate/Ni seed layer (~30 nm) from an electrolyte containing 0.11 M cobalt sulphate, 0.91 M nickel sulphate, 0.17 M nickel chloride, 0.48 M boric acid, 0.29 M sodium hypophosphite, and 0.1 g sodium dodecyl sulphate [9]. All electrochemical experiments were carried out in a conventional dual electrode cell without agitation at room temperature. A nickel plate with area of 2 cm^2 was used as the anode. The duty ratio for the positive pulse current is 1 : 5 and that for the negative pulse current is 1 : 10, respectively. The total deposition time was 30 minutes.

The as-deposited films were heat treated at 673 K for 4 h in a vertical furnace with a protective atmosphere of high purity argon, which was placed inside a superconducting magnet of up to 12 T, and then cooled down to room temperature. The direction of the external magnetic field is perpendicular to the surface of the films; the magnetic flux density of the applied magnetic field during the annealing process was 0 T, 6 T, and 12 T, respectively. Each magnetic field annealing experiment was conducted twice to make sure that the result was reproducible from sample to sample.

Field emission scanning electronic microscopy (FE-SEM, SUPRA 35, Japan) was carried out to detect the surface morphology of the Co-Ni-P alloy thin films. Grazing Incidence X-Ray Diffraction (GI-XRD, Ultima IV, Japan) measurements were performed using Cu Kα radiation (40 kV, 40 mA, $\lambda = 1.57$ Å). The mechanical properties of the films, that is, Nanohardness and Young's modulus, were measured by nanoindentation method (TriboIndenter-900, USA) with a diamond tip and using a mechanical tester with the pressure and displacement of 1980 nN and 120 nm, respectively. Each sample was indented with at least 10 indents in order to ensure statistical viability. The magnetic properties of the samples before and after annealing with and without high magnetic fields were investigated using vibrating sample magnetometer (VSM, lakeshore 7407, USA).

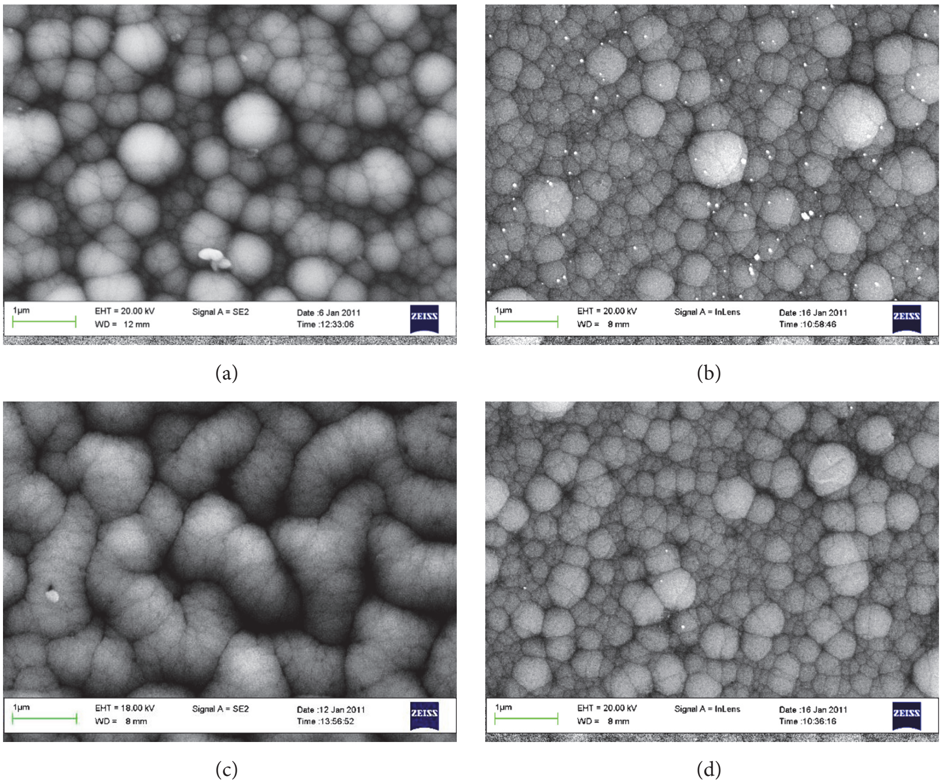
3. Results and Discussion

3.1. Morphology of Co-Ni-P Films. In Figure 1, surface morphologies of the as-deposited Co-Ni-P film and the annealed film with and without high magnetic fields were observed by FE-SEM.

It is apparent that not only the morphology of the as-deposited film differs from the annealed case, but also a remarkable difference can be found in the morphology of the annealed films with and without a magnetic field. The as-deposited film with a rough surface shown in Figure 1(a) consisted of the grape-like spherical clusters, which were Co-based solid solution cell with high content of Ni and P formed under a higher overpotential. After being annealed at 673 K, the surface of the film (Figure 1(b)) was changed into smooth and the grain size became more uniform comparing with Figure 1(a). The white dots in Figure 1(b) were phosphorus grains separated out from the alloy, where dots disappeared when a 6 or 12 T magnetic field was applied during annealing process. For the case of annealing at 6 T, as Figure 1(c) displays, the small polyhedral cell coalesced together to form an intestine-like appearance with the spherical clusters vanishing. Finally, the film obtained under a 12 T high magnetic heat treatment (Figure 1(d)) showed grain size and morphology similar to the annealed sample without a magnetic field (Figure 1(b)).

The initial as-deposited films with nonuniform grain growth and roughness are consumed by the diffusion during the annealing process to form a relative uniform film. However, double different types of annealed microstructures were obtained in the Co-Ni-P films with the application of 6 T and 12 T magnetic fields. It does not exactly determine which mechanism is responsible for evolution of the surface morphology, but it may be attributed to two factors. One is the coalescence of the grains with similar starting orientation induced by the polarized effect [20, 21] of a moderate magnetic field (6 T). The magnetic moment in these ferrite grains induced by the applied uniform magnetic field results in the grains attracting each other. This kind of polarized effect could reduce the total energy of the whole system. The other is that magnetic materials and paramagnetic materials will be affected by a paramagnetic force [22], $\chi_m B^2 \nabla c / 2\mu_0$ (where χ_m is the susceptibility, B is the magnetic flux density, c is the concentration, and μ_0 is the vacuum permeability), which as a pulling force can improve the diffusion of components [23, 24]. The fact that the accelerating effects of a 12 T strong magnetic field on the diffusion process are a larger contribution against the polarized effect is of benefit to formation of more uniform morphology with smaller grain size in the Co-Ni-P films as shown in Figure 1(d).

3.2. Structure and Texture of the Films. XRD patterns of all Co-Ni-P films were illustrated in Figure 2. The diffraction



(a) (b) (c) (d)

FIGURE 1: FE-SEM micrographs of the pulsed-electrodeposited Co-Ni-P films before annealing (a) and magnetic annealing in the case of (b) $B = 0$ T, (c) $B = 6$ T, and (d) $B = 12$ T.

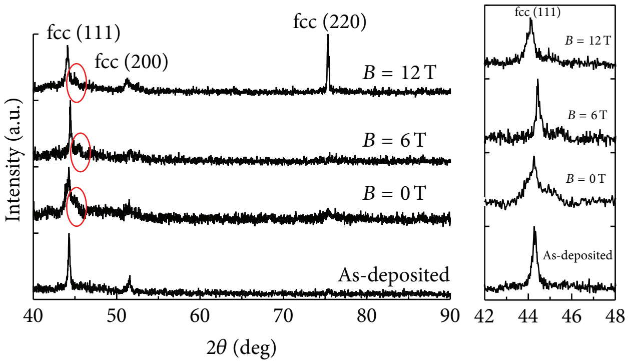


FIGURE 2: XRD patterns of Co-Ni-P films: (a) as-deposited and annealed at 673 K for 4 h in a magnetic field of (b) $B = 0$ T, (c) $B = 6$ T, and (d) $B = 12$ T. The right side was the amplified zone at the angular position from $2\theta = 42^\circ$ to 48°.

peaks of (111), (200), and (220) before and after magnetic field annealing demonstrated the formation of fcc structure in Co-Ni-P alloys. The amplified zone at the angular position from $2\theta = 42^\circ$ to 48° reveals that the as-deposited film exhibits only α (fcc) phase. However, diffraction peak curve bread caused by phosphide phase (CoP or NiP) around $2\theta = 45^\circ$ has been detected for the postannealed films. This phenomenon can be explained as follows: the EDS (Energy Dispersive Spectrometer) results showed that the composition of both the as-deposited and the annealed Co-Ni-P films was $Co_{37}Ni_{47}P_{16}$ (atom percentage with 1.5% error). The high magnetic field annealing shows no effects on composition of Co-Ni-P films. Numerous works have indicated that a phosphide phase appears at around 15 at% P [2]. The supersaturated α (fcc) phase solid solution was formed as the highly current density of pulse-electrodeposition technology; after annealing, amount of P and parts of Co and Ni were separated out of the Co-based solid solution (α phase) resulting in the formation of Co-rich CoNiP phosphide phase.

For the case of annealing at 6 T, the Co element from the Co-rich CoNiP phosphide phase incorporated into the Ni lattice and formed a Co-poor CoNiP phosphide phase, which led to a right-direction shift of the α phase [25]. However, as the magnetic field was increased to 12 T, the diffraction peak of Co-rich CoNiP phosphide phase has been detected and the 2θ-position was different compared with the film annealed without applied magnetic field. Meanwhile, the diffraction peak of CoNiP phosphide phase became narrow after being annealed under the external field. The evolution of 2θ-position and width of phosphide phase's diffraction peak may be caused by the reason that the diffusion of Co and P elements was strongly depending on the magnetic flux density [22, 23]. Compared with the visible (200) and (220) peaks, (111) texture is predominant for the as-deposited film, the film annealed at $B = 0$ T, and the film annealed at $B = 6$ T magnetic field. However, as the magnetic field was increased to 12 T, the drastic increase in the intensity of (220) texture indicates that the preferred orientations in the films are (220).

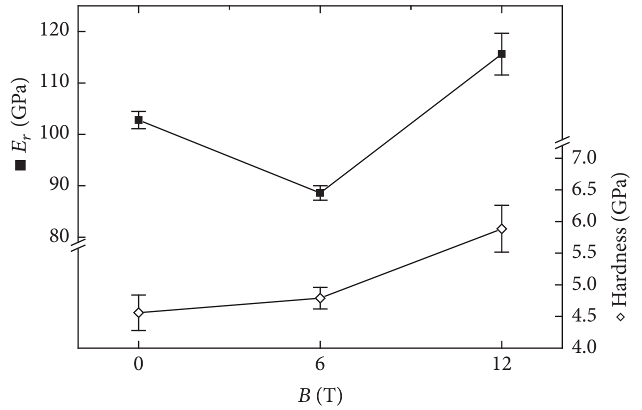


Figure 3: Dependence of the Nanohardness and Young's modulus on the magnetic flux density (B) applied for Co-Ni-P films during annealing.

Table 1: Coercivity field (H_c) and saturation magnetization (M_s) of Co-Ni-P films before and after magnetic field annealing.

Co-Ni-P films	(H_c) (Oe)	(M_s) (memu/cm^2)
(a) As-deposited	84.611	79.86
(b) Annealed under 0 T	442.58	221.60
(c) Annealed under 6 T	621.33	113.15
(d) Annealed under 12 T	471.28	149.64

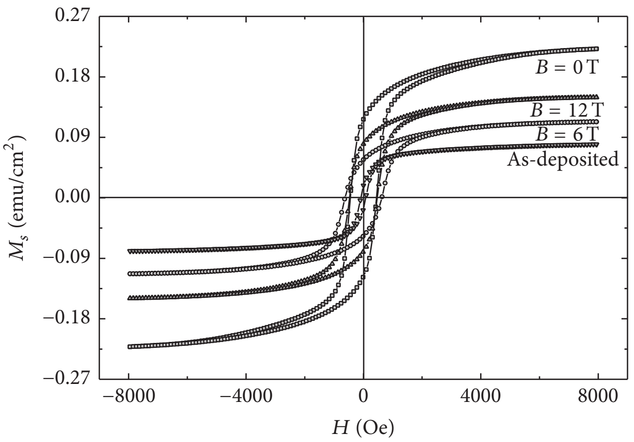


Figure 4: The in-plane hysteresis loops of as-deposited Co-Ni-P film and of the films annealed at 673 K for 4 h under 0 T, 6 T, and 12 T magnetic field conditions.

It can be summarized that the texture evolution of annealed Co-Ni-P film is closely related to magnetic flux density.

Based on XRD results, the average lattice constant of the as-deposited film was determined by using Bragg Equation to be 3.542 Å. In the case of the films annealed with $B = 0$ T, 6 T, and 12 T, the mean lattice constant is 3.544 Å, 3.528 Å, and 3.549 Å, respectively. A markedly decrease in the lattice constant happens in case of the film annealing with a 6 T magnetic field. The release of internal stress in supersaturated α (fcc) phase solid solution during annealing process may lead to the change of lattice constant. More perhaps, the content of Co elements in Ni lattice also decreases the lattice constant of Co-Ni-P alloy films. This phenomenon correlates well with the observed microstructural changes, proving again that the moderate magnetic field annealing makes more Co incorporated into Ni lattice.

3.3. Mechanical Properties of the Films. As shown in previous sections, the application of high magnetic fields during annealing process influences the morphology and microstructure of the electrodeposited Co-Ni-P films. Thus, it is expected that the mechanical and magnetic properties should be affected by magnetic fields as well. Figure 3 shows the dependence of Nanohardness and Young's modulus (E_r) of the annealed films on the magnetic flux density.

It is apparent from Figure 3 that the magnetic flux density increasing increases the hardness of the films. For E_r, a minimum is observed for $B = 6$ T and the highest value is obtained for $B = 12$ T. The increase in the Nanohardness may be caused by the change of internal stress state of the films due to magnetoelastic interaction [26]. The influence of high magnetic fields on the lattice state of the films plays a significant role in Young's modulus.

3.4. Magnetic Properties of the Films. The magnetic properties, measured by VSM with the magnetic field along the plane of the film (Figure 4), the coercivity field (H_c), and the saturation magnetization (M_s) of the films before and after annealing at different magnetic field conditions are summarized in Table 1. Despite of a magnetic field, annealing process significantly increases H_c and M_s of the films. It has to be noticed that the coercivity field reaches a maximum value equal to 621.33 Oe and the saturation magnetization falls to the minimum at 113.15 memu/cm^2 when the film was annealed under an external magnetic field of 6 T.

The coercivity field (H_c) of Co-Ni-P films increased after being annealed, which was caused by the increasing of surface particle size. The maximum H_c was obtained at 6 T maybe due to the intestine-like appearance which was coalesced by amount polyhedral cells. The saturation magnetization of Co-Ni-P films was determined by the magnetic phases of alloy films. The as-deposited Co-Ni-P was a kind of supersaturated solid solution with high content of P; thus, its saturation magnetization was relatively lower [27]. The phosphide is separated out of solid solution after being annealed and the saturation magnetization after being annealed. Comparing the three annealing samples with and without a high magnetic field, the saturation magnetization of Co-Ni-P films was depended on the Co content in fcc-phases. When annealed under high magnetic field, the Co incorporated into Ni lattice (phosphide) and the saturation magnetization decreased. As more Co incorporated into Ni lattice at 6 T, its saturation magnetization was the minimum in the annealed Co-Ni-P films. Since there is still open question concerning the influence mechanism of high magnetic field during the annealing process on the microstructure and properties of the Co-Ni-P films, some future investigations should be undertaken.

4. Conclusions

Pulsed-electrodeposited Co-Ni-P films were annealed in a high magnetic field to investigate the magneto-induced modification of the morphology, texture, and properties. The results indicated that two distinct types of annealed microstructures were obtained in the Co-Ni-P films with the application of 6 T and 12 T magnetic fields. The obtained lattice constants from XRD results were corresponding to the shift of the (111) peaks, reflecting that more Co incorporated into Ni lattice under a 6 T magnetic field annealing. In comparison with the annealing without and with a 12 T magnetic field (in the absence and presence of a 12 T magnetic annealing), the coercivity field reaches the maximum, and the saturation magnetization falls to the minimum in case of $B = 6\,\mathrm{T}$.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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References

[1] M. Srivastava, V. K. W. Grips, and K. S. Rajam, "Electrodeposition of Ni-Co composites containing nano-CeO_2 and their structure, properties," *Applied Surface Science*, vol. 257, no. 3, pp. 717–722, 2010.

[2] D.-Y. Park, N. V. Myung, M. Schwartz, and K. Nobe, "Nanostructured magnetic CoNiP electrodeposits: structure-property relationships," *Electrochimica Acta*, vol. 47, no. 18, pp. 2893–2900, 2002.

[3] M. Uhlemann, A. Krause, J. P. Chopart, and A. Gebert, "Electrochemical deposition of co under the influence of high magnetic fields," *Journal of the Electrochemical Society*, vol. 152, no. 12, pp. C817–C826, 2005.

[4] S. Guan and B. J. Nelson, "Pulse-reverse electrodeposited nanograinsized CoNiP thin films and microarrays for MEMS actuators," *Journal of the Electrochemical Society*, vol. 152, no. 4, pp. C190–C195, 2005.

[5] S. M. Spearing, "Materials issues in microelectromechanical systems (MEMS)," *Acta Materialia*, vol. 48, no. 1, pp. 179–196, 2000.

[6] T. Homma, M. Suzuki, and T. Osaka, "Gradient control of magnetic properties in electroless-deposited CoNiP thin films," *Journal of the Electrochemical Society*, vol. 145, no. 1, pp. 134–138, 1998.

[7] Z. Q. Zou, H. Wang, J. Zhou, D. F. Shen, and Y. P. Lee, "Influence of Ni content on the microstructure and magnetic and magneto-optical properties of sputtered (Co1-xNix)Pt 3 alloy films," *European Physical Journal B*, vol. 45, no. 1, pp. 97–102, 2005.

[8] M. S. Chandrasekar and M. Pushpavanam, "Pulse and pulse reverse plating-conceptual, advantages and applications," *Electrochimica Acta*, vol. 53, no. 8, pp. 3313–3322, 2008.

[9] K. S. Lew, M. Raja, S. Thanikaikarasan, T. Kim, Y. D. Kim, and T. Mahalingam, "Effect of pH and current density in electrodeposited Co-Ni-P alloy thin films," *Materials Chemistry and Physics*, vol. 112, no. 1, pp. 249–251, 2008.

[10] V. Georgescu and M. Daub, "Magnetic field effects on surface morphology and magnetic properties of Co-Ni-P films prepared by electrodeposition," *Surface Science*, vol. 600, no. 18, pp. 4195–4199, 2006.

[11] A. Levesque, S. Chouchane, J. Douglade, R. Rehamnia, and J.-P. Chopart, "Effect of natural and magnetic convections on the structure of electrodeposited zinc-nickel alloy," *Applied Surface Science*, vol. 255, no. 18, pp. 8048–8053, 2009.

[12] K. Theeratatpong, S. Danchaivijit, and Y. Boonyongmaneerat, "Effects of Co content and heat treatment on mechanical properties of electrolessly deposited Ni-Co-P alloys," *Surface and Interface Analysis*, vol. 46, no. 4, pp. 276–282, 2014.

[13] C. Ma, S. C. Wang, L. P. Wang, F. C. Walsh, and R. J. K. Wood, "The electrodeposition and characterisation of low-friction and wear-resistant Co-Ni-P coatings," *Surface and Coatings Technology*, vol. 235, pp. 495–505, 2013.

[14] C. You, Z. D. Zhang, C. Yang, X. K. Sun, W. Liu, and X. G. Zhao, "The effect of magnetic heat treatment on exchange interaction and magnetic properties of Sm-Co/$Fe_{65}Co_{35}$ multilayered films," *Journal of Alloys and Compounds*, vol. 366, no. 1-2, pp. 94–100, 2004.

[15] G. Youhui, Z. Jinghan, W. Yuqing, E. B. Park, and C. J. Yang, "The nucleation process and magnetic interaction in nanocrystalline alloy $Nd_4Fe_{77}Co_3B_{16}$," *Journal of Applied Physics*, vol. 84, no. 8, pp. 4388–4393, 1998.

[16] Y. B. Li, Y. F. Lou, L. R. Zhang, B. Ma, J. M. Bai, and F. L. Wei, "Effect of magnetic field annealing on microstructure and magnetic properties of FePt films," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 23, pp. 3789–3791, 2010.

[17] A. Markou, I. Panagiotopoulos, and T. Bakas, "Effects of layering and magnetic annealing on the texture of CoPt films," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 22, pp. L61–L63, 2010.

[18] X. Zhang, D. Wang, S. Zhang et al., "Effect of high magnetic field annealing on the microstructure and magnetic properties of CoFe layered double hydroxide," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 20, pp. 3023–3027, 2010.

[19] D. Li, Q. Wang, G. Li, X. Ma, K. Nakajima, and J. He, "Reactive diffusion at the liquid Al/solid Cu interface in a high magnetic field," *Materials and Manufacturing Processes*, vol. 26, no. 6, pp. 821–825, 2011.

[20] G. D. Hibbard, K. T. Aust, and U. Erb, "Thermal stability of electrodeposited nanocrystalline Ni-Co alloys," *Materials Science and Engineering A*, vol. 433, no. 1-2, pp. 195–202, 2006.

[21] K. Wang, Q. Wang, C. Wang, Y. Yuan, C. Liu, and J. He, "Mechanism of formation of aligned two-phase microstructure in a Fe-0.25wt%C alloy under high magnetic field gradients," *Philosophical Magazine Letters*, vol. 89, no. 11, pp. 695–700, 2009.

[22] J. M. D. Coey and G. Hinds, "Magnetic electrodeposition," *Journal of Alloys and Compounds*, vol. 326, no. 1-2, pp. 238–245, 2001.

[23] T. Liu, D. Li, Q. Wang, K. Wang, Z. Xu, and J. He, “Enhancement of the Kirkendall effect in Cu–Ni diffusion couples induced by high magnetic fields,” *Journal of Applied Physics*, vol. 107, no. 10, Article ID 103542, pp. 1–3, 2010.

[24] D. Li, K. Wang, Q. Wang, X. Ma, C. Wu, and J. He, “Diffusion interaction between Al and Mg controlled by a high magnetic field,” *Applied Physics A: Materials Science and Processing*, vol. 105, no. 4, pp. 969–974, 2011.

[25] L. Tian, J. Xu, and C. Qiang, “The electrodeposition behaviors and magnetic properties of Ni-Co films,” *Applied Surface Science*, vol. 257, no. 10, pp. 4689–4694, 2011.

[26] J. A. Koza, F. Karnbach, M. Uhlemann et al., “Electrocrystallisation of CoFe alloys under the influence of external homogeneous magnetic fields-Properties of deposited thin films,” *Electrochimica Acta*, vol. 55, no. 3, pp. 819–831, 2010.

[27] D. Pan and D. Turnbull, “Magnetic properties of amorphous co-p alloys,” *Journal of Applied Physics*, vol. 45, no. 3, pp. 1406–1412, 1974.