Effect of Heat-Treatment On Magnetic Properties of Electroless Ni-B Films

By T. Saito, E. Sato, M. Matsuoka & C. Iwakura

The effect of heat treatment on the magnetic properties of electroless Ni-B films (0.5-5 wt pct B) was examined with reference to electrodeposited Ni film. The coercivity, saturation magnetic flux density and residual magnetic flux density of the Ni-B films were measured using a vibrating sample magnetometer. Changes in magnetic properties of the films with boron content and heat treatment temperature are discussed on the basis of the crystallite size of ferromagnetic fcc Ni and the amount of precipitated paramagnetic Ni_3B. It is concluded that precise control of boron content and heating temperature is essential in producing an improved soft magnetic thin film.

Table 1
Bath Composition & Operating Conditions For Electroless Ni-B Plating

Chemicals	Concentration (mol/dm^3)		
	Ni-0.5B	Ni-3B	Ni-5B
$NiSO_4 \cdot 6H_2O$	0.10	0.10	0.10
$Na_3C_6H_2O_7 \cdot 2H_20$	—	—	0.10
$Na_2C_3H_2O_4 \cdot H_2O$	—	—	0.10
$C_4H_4O_6$	0.05	0.20	—
$C_4H_5O_4$	0.20	—	—
CH_2NH_2COOH	0.20	—	—
$(CH_3)_2NH \cdot BH_3$	0.05	0.05	0.05
pH	6.5	6.0	6.0
Temperature	60 °C	60 °C	60 °C

Electroless plating is the well-known wet process for producing a thin magnetic film on both conducting and nonconducting substrates. Hard magnetic Co-P films have been prepared by electroless plating, using hypophosphite as a reducing agent and widely employed as magnetic recording media.[1-4] On the other hand, soft magnetic electroless Co-B films are also deposited by using dimethylamine borane and they are potential candidates for magnetic head applications.[5,6] Nickel-based films are beneficial from the economical point of view, however, in fabricating non-magnetic or soft magnetic materials because of the reasonable price of nickel compared to cobalt. For example, electroless Ni-P films with 10 wt pct P or above have been used as a non-magnetic undercoat in producing hard disks.[7] Intensive research related to soft magnetic Ni-Fe-P films has been performed to get high-saturation magnetization and low coercivity.[8-10] Such magnetic properties are in demand for fabricating a magnetic head with this type of thin film.[11] Regrettably, there have been few studies of the magnetic properties of electroless Ni-B films.

In this study, electroless Ni-B films containing 0.5-5 wt pct B were prepared by using dimethylamine borane as a reducing agent. Their magnetic properties were examined to develop a reasonable process for producing soft magnetic films. Because the magnetic properties were very sensitive to the crystal state of the deposits and the magnetic moment of the constituent materials, the effects of the precipitation of Ni_3B and the apparent crystallite size of fcc Ni on the magnetic properties were systematically investigated as a function of the boron content of the films and heating temperature.

Experimental Procedure

Bath composition and operating conditions for electroless Ni-B plating are shown in Table 1. Three kinds of electroless nickel plating baths were employed in preparing Ni-0.5 wt pct B, Ni-3 wt pct B and Ni-5 wt pct B films. For comparison, pure Ni film was also electroplated from the conventional Watts nickel bath. As-purchased special grade chemicals and distilled water were used in making up the plating solutions. Copper wire with a purity of 99.99 percent (0.5 mmϕ x 100 mm) was used as a substrate for depositing Ni and Ni-B films.

The composition of the films was analyzed by atomic absorption spectrometer after dissolving them in 1 mol/dm^3 nitric acid solution. The thickness of the films was calculated from the weight gain from plating and also measured, using an X-ray fluorescence thickness meter. The crystal structure of the films was analyzed using an X-ray diffractometer. An apparent crystallite size of the films was calculated from Scherrer's equation:[12]

$$D = 0.9\lambda/\beta 1/2 \cdot \cos\theta \qquad (1)$$

where λ is the wave length of CuKα radiation, $\beta 1/2$ is the half-width of the diffraction line and θ is the diffraction angle.

Magnetic properties were measured using a vibrating sample magnetometer equipped with a compensation circuit against geomagnetism. Heat treatment of the films was carried out at different temperatures in vacuum (10^{-3} Pa) for one hr, after raising the temperature at a rate of 278 °K/min to a given value.

Results & Discussion

Crystal Structure of As-deposited & Heat-treated Ni-B Films

Typical X-ray diffraction patterns of electrodeposited Ni and electroless Ni-B films with O.5 wt pct B, 3 wt pct B and 5 wt pct B are shown in Fig. 1. In the case of electrodeposited Ni, three diffraction peaks corresponded to Ni(111), Ni(200) and Ni(220) planes. For the electroless Ni-0.5 wt pct B film, the

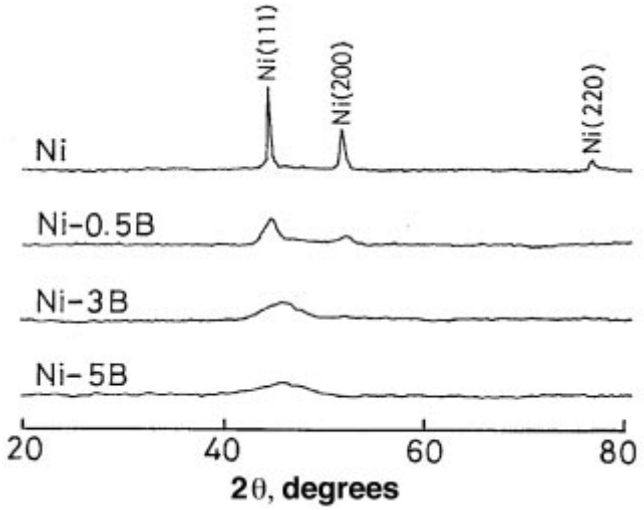

Fig. 1—X-ray diffraction patterns of Ni and Ni-B films before heat treatment.

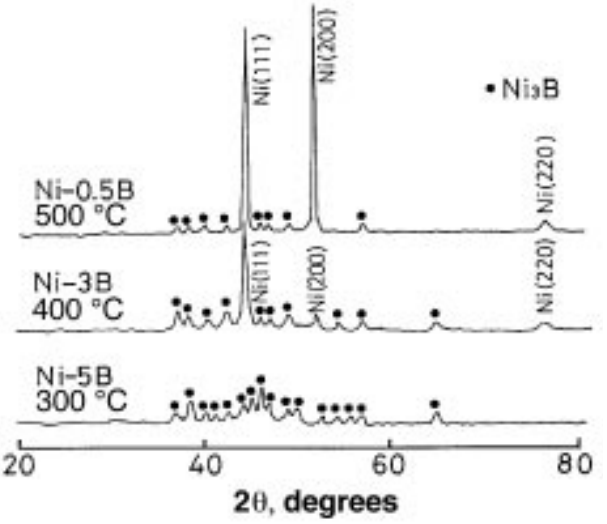

Fig. 2—X-ray diffraction patterns of electroless Ni alloy films after heat treatment.

Ni(220) peak disappeared and only broadened Ni(111) and Ni(200) peaks were detected. In addition, both diffraction peaks shifted to a higher degree, indicating that the fcc Ni lattice would be constricted by the codeposition of boron. Further increase in boron content of Ni-B films gave rise to a single broader peak near $2\theta = 45°$ and the diffraction angle shifted (increased). The broadening of the peaks is mainly attributable both to microstresses and microcrystalline structure or amorphous structure of Ni-B films being supersaturated with respect to boron. Because a sharp line between these structures could not be drawn in this study, apparent crystallite size was calculated from Scherrer's equation, using the half-width of the diffraction peak appearing where 2θ was about 45°.

Typical X-ray diffraction patterns of heat-treated electroless Ni-B films are shown in Fig. 2. Diffraction peaks of Ni and Ni_3B are clearly recognized from the heat-treatment at temperatures above 300 °C. The measured diffraction peaks are in good agreement with data reported for orthorhombic Ni_3B with lattice parameters a, 4.392; b, 5.223; and c, 6.615 Å.[13] The intensity of diffraction peaks ascribed to fcc Ni decreased with increasing boron content of the films; the peaks disappeared at 5 wt pct B. Because the 5 wt pct boron content in Ni-B corresponded to 22.2 at pct, 11.2 at pct Ni should remain even after Ni_3B formation. The existing 11.2 at pct Ni seems therefore to be dispersed in the predominant Ni_3B matrix (88.8 at pct). The formation of Ni_3B was detected at 500, 400 and 300 °C for Ni-0.5 wt pct B films, Ni-3 wt pct B films and Ni-5 wt pct B films, respectively (*i.e.*, the temperature of boride formation decreased with increasing boron content of the films). The same tendency was reported in the system of Ni-P alloys (*i.e.*, the higher the phosphorus content, the lower the temperature of Ni_3P formation.[14]

Apparent crystallite size obtained from Scherrer's equation and lattice constant of the Ni and Ni-B films are summarized in Table 2 as a function of heating temperature. Under the as-deposited condition, the crystallite size of Ni-B films decreased from 80 to 10 Å with increasing boron content and was substantially smaller than that of Ni (400 Å). The crystallite size of Ni-B films increased up to 300 Å, however, with increasing heat treatment temperature. On the other hand, the lattice constant of as-deposited Ni-B films decreased with increasing boron content, but the lattice constant of heat-treated films increased with increasing temperature.

Magnetic Properties of Ni-B Films

The effect of heat treatment on the magnetic properties of electrodeposited Ni and electroless Ni-B films was examined by measuring saturation magnetic flux density (B_s), residual magnetic flux density (B_r) and coercivity (H_c). In the preliminary experiment, the dependence of magnetic properties on film thickness was determined. Saturation magnetic flux density and residual magnetic flux density increased with increasing thickness up to 2 μm and became almost constant with further increase in thickness. The coercivity of the films decreased remarkably in the region from 0.3 to 1.0 μm, then increased slightly with increasing thickness up to 2 μm, but became almost constant with further increase in thickness. In the ensuing experiment, therefore, magnetic properties independent of thickness were determined for the three kinds of Ni-B films as a function of temperature.

Coercivity of Ni-B films

Coercivities of Ni and Ni-B films with a thickness of 2-3 μm are shown in Fig. 3 as a function of temperature. The coercivity of Ni and Ni-B films decreased with increasing temperature up to 300 °C. The sharpness of diffraction peaks corresponding to Ni(111) and Ni(200) planes was increased by the heat treatment, as described in the previous section. Changes in coercivity, therefore, are reasonably explained by the relaxation of internal stress of the films. Heat treatment at temperatures higher than 300 °C caused remarkable increases in coercivity, depending on boron content of the films. The maximum value of H_c appeared at lower temperature with increasing boron content. For example, the coercivity of Ni-5 wt pct B film heat-treated at 500 °C was five times larger than that of an as-deposited film. The increase in H_c seems to be induced by the restricted motion of the magnetic domain walls, because both the precipitation of Ni_3B and the strain incidental to it increase the heterogeneity of the films. After the precipitation of Ni_3B, relaxation of the strain occurs effectively at higher temperature, leading to decreases in the value of H_c. The dependence of the maximum H_c value on boron content is somewhat complex, be-

Table 2
Lattice Constant & Crystallite Size of Ni & Ni-B Films Heat-Treated at Different Temperatures

Kind of films	Heat-treatment temperature, °C	Grain size Å	Lattice constant, Å
Ni	RT~500	400	3.525
	600	400	3.528
	800	400	3.583
Ni-0.5B	RT~300	80	3.524
	400	250	3.525
	500	300	3.525
	600	300	3.528
	800	300	3.586
Ni-3B	RT	15	3.520
	300	25	3.520
	400	150	3.525
	600	300	3.528
	800	300	3.546
Ni-5B	RT	10	3.515

cause the temperature of Ni_3B formation and relaxation of the strain are dependent on the boron content of the films.

Saturation magnetic flux density of Ni-B films

The effect of heat-treatment temperature on the saturation magnetic flux density (B_s) of Ni-B films is shown in Fig. 4. The B_s values of as-deposited Ni and Ni-0.5 wt pct B films were 0.62 T and 0.37 T, respectively. Because the Ni-0.5 wt pct B film is a solid solution of boron dissolved in fcc Ni, ferromagnetism is apparent. Further increase in boron content of the films as in the case of Ni-3 wt pct B and Ni-5 wt pct B decreased the B_s value less than 0.001 T. As-deposited NiB films with boron content greater than 3 wt pct are therefore substantially non-magnetic. Because the Ni-3 wt pct B and Ni-5 wt pct B films are very fine polycrystalline solid solutions, bordering on amorphous or a liquid-like metastable structure, the fcc Ni phase is no longer detectable by X-ray diffraction. Under these conditions, the ferromagnetic property disappears, because the 3d orbital vacancy of nickel is filled by the electrons released from boron atoms.

The saturation magnetic flux density of the heat-treated Ni film at temperatures less than 500 °C was almost constant, but it decreased remarkably at temperatures higher than 600 °C. The same tendency was observed for the Ni-B films heat-treated at 600 °C or above. X-ray analysis indicated the evidence of non-magnetic $Cu_{3.8}Ni$ formation under such conditions, as a consequence of the thermal diffusion of copper from the substrate, which is partly attributed to an increase in the lattice constant of the films, as shown in Table 2. On the other hand, the dependence of the value of B_s value on heat treatment at temperatures less than 500 °C was quite different as boron content of the films varied. The B_s value of the Ni-0.5 wt pct B film gradually increased with increasing temperature, attributed to the crystal growth of fcc Ni. The maximum value of B_s for the Ni-0.5 wt pct B film was considerably smaller than that of electrodeposited Ni as the result of the precipitation of paramagnetic Ni_3B.[15] The B_s value of Ni-3 wt pct B film was substantially increased by heat-treatment at a temperature region where a solid solution transformed into fcc Ni and Ni_3B phases. By contrast, the B_s value of the Ni-5 wt pct B films became negligibly small by heat treatment at temperatures higher than 300 °C because a small amount of nickel was dispersed in the Ni_3B matrix. Consequently, the B_s value is increased by the formation of a fcc Ni phase, but decreased by the precipitation of Ni_3B.

The magnetic properties of heat-treated Ni-B films prepared from an electroless ethylenediamine bath using sodium borohydride as a reducing agent were examined by Gorbunova *et al.*[16] They also reported the similar maximum behavior in H_c and B_s values, but the effect of boron content on the magnetic properties was somewhat different from our results. Bath formulation of electroless Ni-B plating is therefore also another important factor in determining the magnetic properties of the films.

Residual magnetic flux density of Ni-B films

Residual magnetic flux density (B_r) of the Ni and Ni-B films is shown in Fig. 5 as a function of heat-treatment temperature. The B_r value of the films decreased with increasing boron content of the films and the dependency of it on temperature was almost the same as the value shown in Fig. 4 (*i.e.*, the higher the B_r value, the higher the B_s value. Although the B_r value of the films is influenced by the magnetic moment of the constituent material and rigidity against the motion of the magnetic domain wall, the similarity between B_r and B_s indicates that the B_r value is strongly influenced by the magnetic moment. The effect of the magnetic domain wall, however, which is sensitive to crystal structure and strain of the films, also contributes to the value of B_s. As a result, the rectangularity defined by B_r/B_s changes with boron content and heat treatment of the films. The maximum rectangularity of about 0.60 was obtained by heating the Ni-3 wt pct B film at 500 °C for one hr. The B_s, B_r and H_c values of the film were found to be O.256 T, O.151 T and 7 kA/m, respectively. Consequently, the precise control of boron content and heating temperature is essential in developing the desired magnetic properties of the Ni-B films.

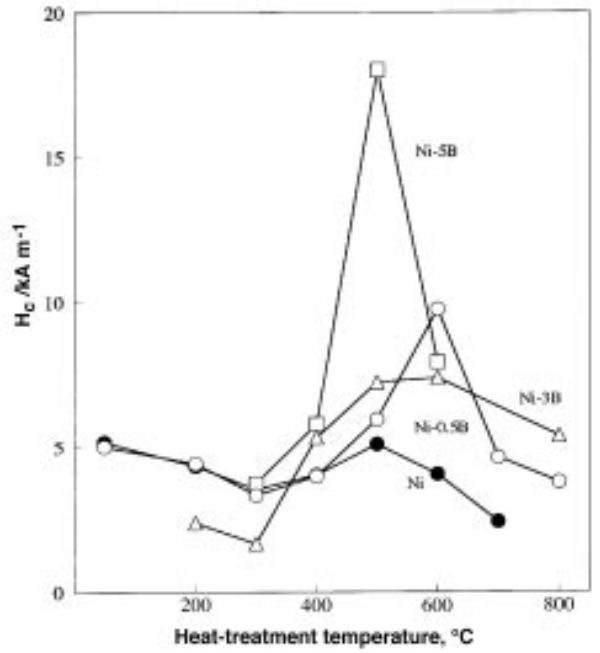

Fig. 3—Effect of heat treatment on coercivity (H_c) of Ni and Ni-B films.

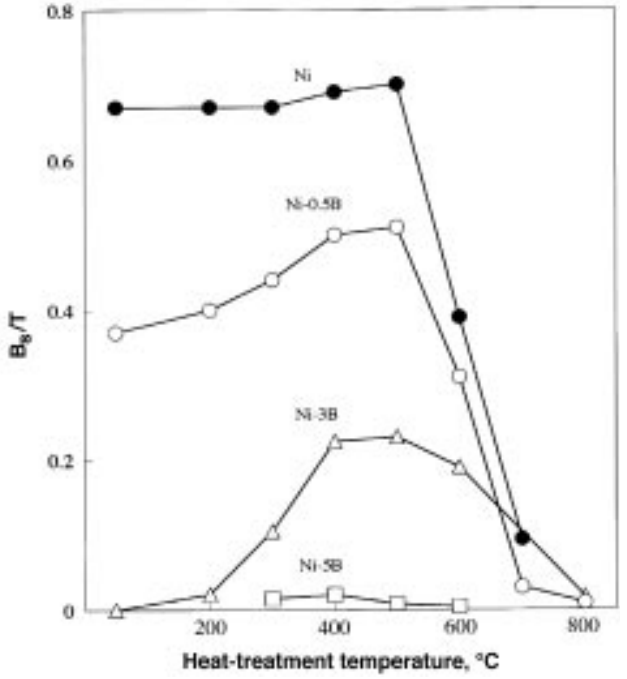

Fig. 4—Effect of heat treatment on saturation magnetic flux density (B_s) of Ni and Ni-B films.

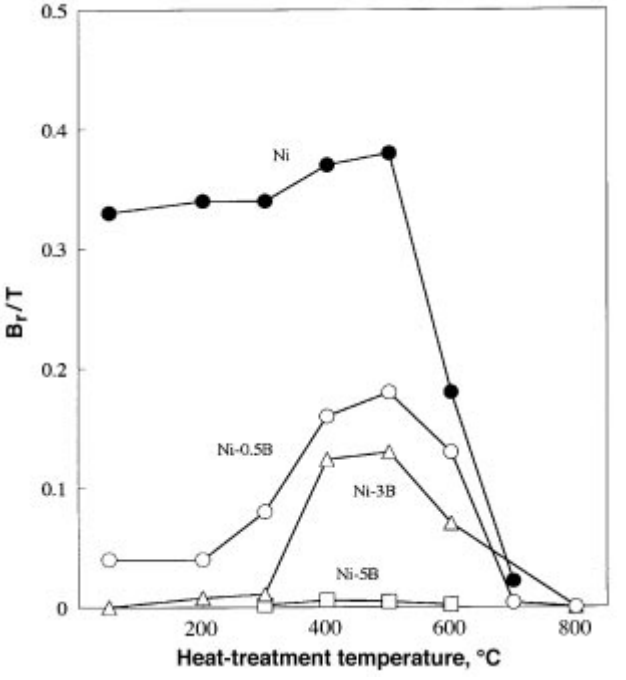

Fig. 5—Effect of heat treatment on residual magnetic flux density (B_r) of Ni and Ni-B films.

Findings

The magnetic properties of electrodeposited Ni and electroless Ni-B films with boron contents of 0.5, 3 and 5 wt pct were measured as a function of heat treatment temperature. Magnetic properties of the films were discussed on the basis of changes in boron content and crystal structure. The results are summarized as follows.

1. Although the Ni-B films with 3 and 5 wt pct B are nonmagnetic, Ni-B film with 0.5 wt pct B is ferromagnetic in nature because of the presence of fcc Ni in the as-deposited condition.
2. Ferromagnetic properties are induced by heat treatment of the Ni-B films as the result of phase separation into fcc Ni and Ni_3B from the solid solution's being supersaturated with respect to boron.
3. In the case of Ni-5 wt pct B films, ferromagnetic properties are no longer detected, even after heat treatment, because a small amount of Ni is dispersed into a paramagnetic Ni_3B matrix.
4. Improved magnetic properties are obtained by heat treatment at temperatures from 27 to 500 °C. Further increases in temperature result in deterioration of magnetic properties because of formation of non-magnetic $Cu_{3.8}Ni$.
5. Superior soft magnetic properties are obtained for Ni-3 wt pct B film by heating at 500 °C for one hr.

Editor's note: *Manuscript received, March 1998.*

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