Microstructure and Magnetic Properties of Electroless Ni-Fe-B Alloy Films

By D. Kim, H. Matsuda, K. Aoki and O. Takano

The objective of this study was to investigate the magnetic properties and microstructure of electroless Ni-Fe-B alloy films deposited in different types of solutions. Soft magnetic films with low coercive force (Hc) and good squareness were obtained in a solution using sodium citrate and/or sodium tartrate as complexing agents. The lowest value of coercive force at 1 µm film thickness indicated 20 A/m, as plated. The alloy films consist of fine-particulate crystallite with high crystallinity.

Soft magnetic thin films of Ni-Fe have been extensively used in the fabrication of magnetic memories[1-4] for information storage in computers using very high speed switching. The alloys are noted for their potential applications to the under-coatings layer of double layer perpendicular recording media,[5-8] thin-film head materials[9] and EMI shielding materials,[10] having high saturation magnetization and high permeability.

We have already described the deposition behavior and solution stability of a new type of electroless Ni-Fe-B plating solution, using dimethylamineborane (DMAB) as a reducing agent.[11] In the current study, we investigated the effect of plating conditions on the magnetic properties and microstructure of electroless Ni-Fe-B alloy films.

Experimental Procedure

The electroless Ni-Fe-B alloy films were deposited from a solution having composition and operating conditions as shown in Table 1. To investigate the effect of plating conditions on magnetic properties and microstructure, metallic ion concentration, DMAB concentration and solution pH were varied. Two materials were used as substrate—copper sheet (0.3 mm thick) was used to determine magnetic properties and X-ray diffraction data. Polyimide film (75 µm) was used for observation with the transmission electron microscope (TEM).

On the basis of preliminary experiments, the plating solutions containing sodium citrate, sodium tartrate or a mixture of both were investigated as the complexing agent. The coercivities of the films were evaluated from the M-H loops under an external magnetic field of 4000 A/m, using a vibrating sample magnetometer. Structural characteristics were examined with an X-ray diffractometer and transmission electron microscope.

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

Component	Concentration, mol/L
Nickel sulfate	0.05
Ferrous sulfate	0.05
DMAB	0.03
Sodium citrate	0.10
Sodium tartrate	0.15
Ammonium sulfate	0.50
pH 9 (with NaOH)	
Temp 90 ˚C	

Magnetic Properties

Comparison of Complexing Agents

Figure 1 shows dependence of coercive force on thickness of deposited films. The films were deposited from solutions using different complexing agents, namely, the single complexing agents sodium citrate or sodium tartrate, and a double complexing agent with both. As shown in Fig. 1, the coercive force (Hc) decreased with increasing thickness of the deposited film. The coercive force of the films deposited in the citrate bath exhibited greater value than that of the tartrate bath or double complexing agent bath. It has already been reported that the solution using tartrate was not sufficient for stability.[10] Accordingly, subsequent investigations will be carried out using the double complexing agent solutions.

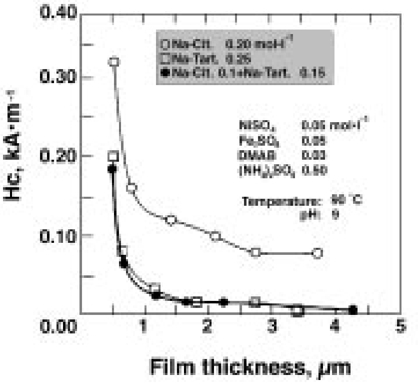

Fig. 1—Effect of film thickness on coercive force.

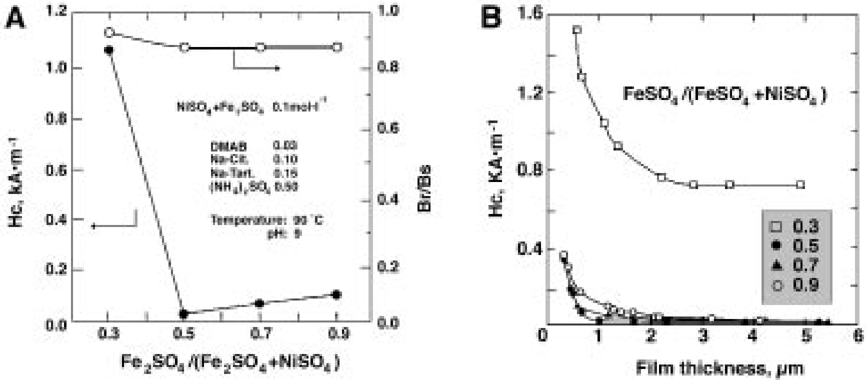

Fig. 2—Effect of metallic salt ratio on magnetic properties.

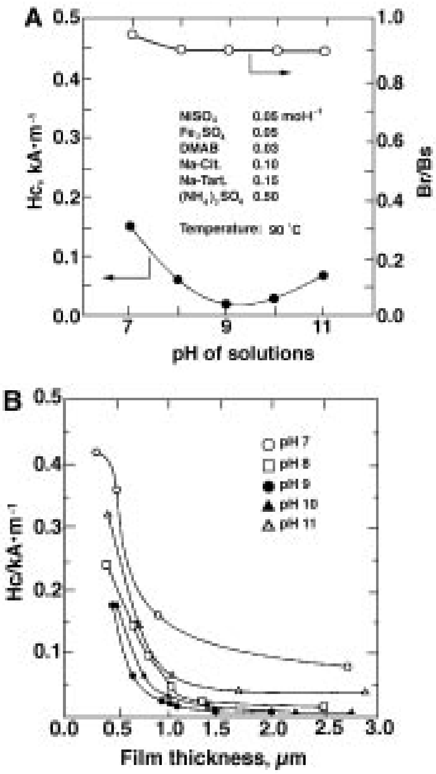

Fig. 3—Effect of solution pH on magnetic properties.

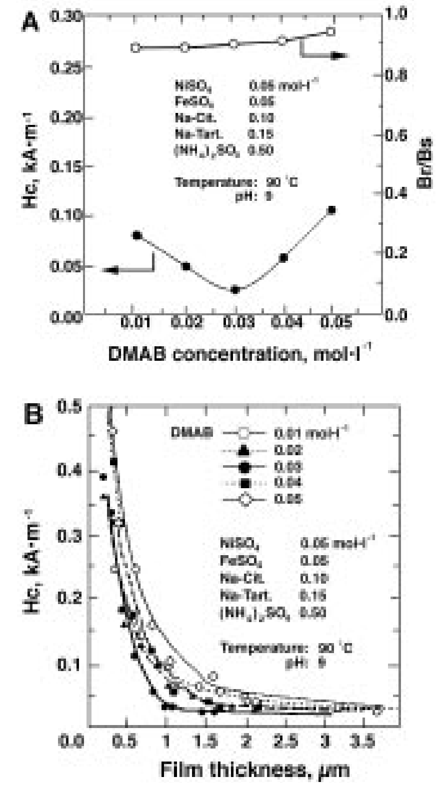

Fig. 4—Effect of DMAB concentration on magnetic properties.

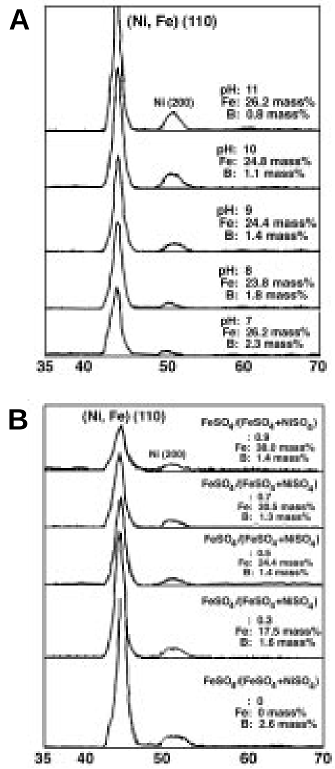

Fig. 5—Changes in X-ray diffraction patterns with (a) metallic salt ratio and (b) solution pH.

Effect of Metallic Salt Ratio

The effect of the metallic salt ratio [$FeSO_4/(FeSO_4 + NiSO_4)$] on the coercive force (Hc) is shown in Fig. 2. In this study, the metallic salt ratio was varied from 0 to 0.9, keeping the concentration of total metallic salt at 0.1 mol/L. As shown in Fig. 2a, the optimum soft magnetic property is found at a metallic salt ratio of 0.5. The squareness (Br/Bs) is almost independent of the metallic salt ratio. The squareness indicates a constantly superior value of about 0.92. As shown in Fig. 2b, for a metallic salt ratio in the solution above 0.5, the coercive force decreases from 400 A/m to 8 A/m as the film thickness increases from 0.3 to 5.4 μm. For solutions with metallic salt ratio above 0.5, the coercive force at film thickness above 2 μm exhibits superior values under 16 A/m.

Effect of pH

The magnetic properties of the films depend on pH, as shown in Fig. 3a. The film thickness effect was observed in solutions of various pH ranges. Figure 3b shows the coercive force as a function of film thickness in various pH ranges. For the range from 7 to 10, the coercive force at the same film thickness decreased with increasing pH. The coercive force of films plated at pH 11, however, indicated higher value than for films plated at pH 8 to 10. The coercive force of a one–μm film plated at pH 9 was determined to be 24 A/m.

Effect of DMAB Concentration

Figure 4 illustrates the effect of DMAB concentration in the solution on the coercive force of the films. As the DMAB concentration increases from 0.01 to 0.03 mol/L, the coercive force decreases from 80 to 24 A/m. Inversely, the coercive force increased at DMAB concentration above 0.03 mol/L. From this result, the optimum DMAB concentration is found to be 0.03 mol/L.

Microstructure

It is apparent that the coercive force is affected by composition and structure of the deposited film. Figure 5a shows representative X-ray diffraction data of Ni-Fe-B films deposited with various metallic salt ratios. The composition of the films deposited in each solution is shown in the figure.

As the metallic salt ratio rises, the peak for a (110) plane of α-(Fe,Ni) is reduced in intensity and the half-width of the diffraction line increases. Reduction of the peak intensity with increasing metallic salt ratio suggests that the crystallite size is decreasing. This change of size corresponds to conversion to fine-particulated crystallite with high crystallinity.

X-ray diffraction data, as a function of solution pH, is illustrated in Fig. 5b. As the solution pH rises, the diffraction peak for (110) plane of α-(Ni,Fe) increases in intensity. The peak for the (200) plane of Ni increases as well. This change seems to be a result of reduction of boron content in the deposited films.

Figure 6 shows typical TEM bright field images and the corresponding THEED patterns. The films were deposited from varied metallic salt ratios from 0.3 to 0.9. As the metallic salt ratio increased, the average crystallite size of the deposited films decreased from 120 to 38 Å. At the metallic salt ratio of 0.5, the optimum condition in terms of magnetic properties, the average crystallite size was 75 Å. The rings of THEED patterns are a result of the fine-particulated crystallite.

(Continued on page 62)

(Continued from page 36)

Table 2
Structural and Magnetic Properties of Electroless Ni-Fe-B Alloy Films

$FeSO_4$/($NiSO_4$+$FeSO_4$) in solution	Film composition, mass%		X-ray diffraction				TEM image	Coercive force (A/m)
	Fe	B	2θ (°)	Lattice spacing (A)	Half width (°)	Apparent crystallite size (A)	Crystallite size (A)	
0.3	17.5	1.6	44.29	2.0435	1.18	73	120	1040
0.5	24.4	1.4	44.27	2.0443	1.28	67	74	24
0.7	30.5	1.3	44.10	2.0518	1.45	59	50	64
0.9	38.0	1.4	44.02	2.0554	1.52	57	38	96

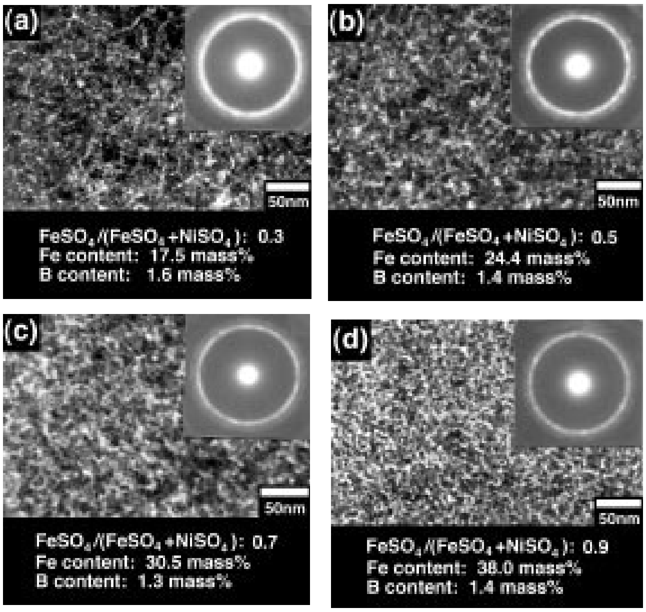

Fig. 6—TEM bright field images of electroless Ni-Fe-B alloy films.

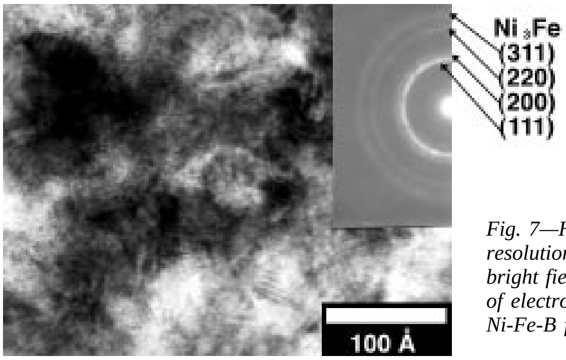

Fig. 7—High-resolution TEM bright field image of electroless Ni-Fe-B film.

Figure 7 shows a high-resolution TEM bright field image of the film deposited under the optimum condition. The lattice spacing ranges from 2.04 to 2.08 Å, which corresponds to the (111) plane of α-Ni_3Fe. From the results of X-ray diffraction data, TEM bright field images and measurement of magnetic properties, the effect of the metallic salt ratio on microstructure and magnetic properties are summarized in Table 2. As the metallic salt ratio increases, Fe content in the deposited films increases; lattice spacing increases as well, but crystallite size decreases with increase of Fe content.

Conclusions

The electroless Ni-Fe-B alloy films deposited in the solution containing a double complexing agent exhibited several excellent soft magnetic properties, such as low coercive force or high squareness. The optimum bath conditions to obtain optimum magnetic properties were as follows; metallic salt ratio of 0.5, DMAB concentration of 0.03 mol/L and pH of 9.

Because the coercive force (Hc) of a one-μm thick film deposited from the optimum bath was 24 A/m, and the squareness of its hysteresis loops indicated superior value, such films are suitable for use in magnetic memories for computer applications or for undercoating of double-layer perpendicular recording media, etc.

The deposited film consists of fine-particulated crystallite with high crystallinity. The crystallite size decreases as the Fe content in the deposited films increases. The crystallite size of the deposited film from the optimum bath was indicated as 75 Å, the film structure owing to onset of soft magnetic properties.

Editor's note: *Manuscript received, July 1994.*

References

1. A.F. Schmeckenbecher, *J. Electrochem. Soc*., **113**, 778 (1966).
2. A.F. Schmeckenbecher, *Plat. and Surf. Fin.*, **58**, 905 (1971).
3. K. Aoki and S. Ishibashi, *J. Met. Fin. Japan*, **21**, 622 (1970).
4. K. Aoki and S. Ishibashi, ibid., **22**, 66 (1971).
5. H. Matsuda and O. Takano, ibid., **38**, 429 (1987).
6. D.H. Kim, H. Matsuda, K. Aoki and O. Takano, *J. Sur. Fin*. Japan, **45**, 202 (1994).
7. H. Matsubara, H. Mizutani, S. Mitamura and T. Osaka, *Trans. IEEE*, Magn., **26**, 1210 (1990).
8. T. Osaka, T. Homma, K. Noda, T. Watanabe and F. Goto, ibid., **27**, 4963 (1991).
9. M. Matsuoka and T. Hayashi, *Plat. and Surf. Fin.*, **69**, 53 (1982).
10. S. Hotta, M. Sugano and H. Honma, *J. Sur. Fin*. Japan, **44**, 217 (1993).
11. D.H. Kim, H. Matsuda, K. Aoki and O. Takano, *Plat. and Surf. Fin*., **83**, 78 (Feb. 1996).

About the Authors

Dr. Dong-Hyun Kim (Department of Materials Science and Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji 671-22, Japan) has studied fabrication of conductor interconnections for microcircuits by means of electroless nickel plating on alumina ceramics. He is a recent PhD graduate of Himeji Institute of Technology.

Dr. Hitoshi Matsuda is an assistant professor at the Metal Surface Engineering Laboratory, Himeji Institute of Technology. He has 18 years' experience in development and application of electroless plating for magnetic recording media. He holds a PhD from Himeji Institute of Technology.

Dr. Koji Aoki is an associate professor at the Metal Surface Engineering Laboratory, Himeji Institute of Technology. His research has been in electroless nickel-phosphorus and its alloys. He holds a BS in applied chemistry from Himeji Institute of Technology and a PhD in electrochemistry from the University of Osaka Prefecture.

Dr. Osamu Takano is a professor in the Metal Surface Engineering Laboratory of Himeji Institute of Technology. He has published many papers on electroless plating and related fields, especially functional finishes, such as magnetic thin films. Dr. Takano received his MS and PhD from Osaka University.