Metastable *bcc* Phase in Sputtered Fe–Ni Alloys

By Kenji Sumiyama*, Masaru Kadono** and Yoji Nakamura*

Fe_{1-x}Ni_x alloy films obtained by the rf sputtering technique have been investigated by X-ray diffraction, magnetization and Mössbauer effect measurements. The single *bcc* phase extends up to about $x=0.4$, a *bcc-fcc* mixed phase appears for $0.4 < x < 0.5$ and a single *fcc* phase predominates for $x > 0.5$. The lattice constants of the *bcc* and *fcc* phases are slightly larger than those of the bulk specimens. As a result of the *bcc* phase extension, both the magnetic moment and the Mössbauer spectrum of the Fe–Ni sputtered alloys change smoothly even in the *bcc-fcc* phase boundary region, in contrast to the results for bulk Fe–Ni alloys.

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I. Introduction

In the Fe–Ni alloy system, the single *bcc* phase is stable up to about 10 at%Ni and the *bcc-fcc* mixed phase appears between 10 and 70 at%Ni at room temperature in its equilibrium phase diagram⁽¹⁾. So far, a metastable *bcc* phase has been considered to be extended up to about 27 at%Ni by conventional air-cooling⁽¹⁾, up to about 30 at%Ni by thermal evaporation⁽²⁾⁽³⁾ and up to about 40 at%Ni by electrodeposition⁽⁴⁾, while a metastable *fcc* phase has been found to be stabilized down to about 30 at%Ni at room temperature in air-cooled alloys⁽¹⁾, down to about 24 at%Ni in rapidly quenched alloys with a very small grain size⁽⁵⁾ and down to about 20 at%Ni in fine powdered alloys⁽⁶⁾.

In the Fe–Mn alloy films produced by the rf sputtering technique, the single *bcc* phase extends up to about 20 at%Mn and its lattice constant is about 0.5% larger than those of the bulk specimens⁽⁷⁾⁽⁸⁾. Since the equilibrium phase diagram of Fe–Ni alloys resembles that of Fe–Mn alloys in the Fe-rich concentration region⁽¹⁾, a similar study has been carried out for the former alloys. The present paper de-

scribes experimental results of X-ray diffraction, magnetization and the Mössbauer effect of the Fe_{1-x}Ni_x sputtered alloy films with $0 \leq x \leq 0.6$ and shows how the single *bcc* phase extends in these films.

II. Experimental Procedures

Ingots of pure Fe and Fe–Ni alloys were prepared from 99.9% pure Fe and 99.9%Ni by arc-melting in an argon atmosphere. Samples were prepared by the rf sputtering on Mylar substrates as described in a previous paper⁽⁷⁾. Here, the deposition rate was about 0.13 nm/s. The composition of sputtered alloy films was determined by the X-ray fluorescence analysis. Since the sputtering rate of Ni atoms is higher than that of Fe atoms, the Ni concentrations of films are about 5–10 at% higher than those of the original targets.

X-ray diffraction patterns were obtained by using Co–K α radiations. A torsion balance magnetometer was used to measure the magnetization at 77 K and 290 K in magnetic fields up to 1.03 MA/m (13 kOe). The Mössbauer effect measurements were carried out at 77 K and 290 K by a constant acceleration type spectrometer, using a ⁵⁷Co source doped with Cu.

III. Results and Discussion

Figure 1 shows low angle parts of X-ray diffraction patterns for the Fe_{1-x}Ni_x sputtered

* Department of Metal Science and Technology, Kyoto University, Kyoto 606, Japan.

** Graduate Student, Department of Metal Science and Technology, Kyoto University, Kyoto 606, Japan. Present address: Sharp Corporation, Nara 632, Japan.

Fig. 1 Low angle parts of X-ray diffraction patterns of the $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys.

Fig. 2 Lattice constant of the $\text{Fe}_{1-x}\text{Ni}_x$ alloys at room temperature. ●: the present sputtered alloys and △: the bulk alloys⁽⁹⁾⁽¹⁰⁾.

alloy films. The broadening of these spectra is due probably to Ar contamination, lattice defects and strains introduced during the sputtering process as well as to a small grain size of the sputtered alloy films⁽⁷⁾. Only the *bcc* peaks were observed for $x < 0.4$, the *bcc* and *fcc* ones for $0.4 < x < 0.5$ and only the *fcc* one for $x > 0.5$. Comparing these results with the equilibrium phase diagram of the Fe-Ni alloys⁽¹⁾, the *bcc*

phase extends to a much higher Ni region in the $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloy films as in the case of $\text{Fe}_{1-x}\text{Mn}_x$ sputtered alloy films⁽⁷⁾⁽⁸⁾.

Figure 2 shows the lattice constants of the *bcc* and *fcc* phases at room temperature derived from several X-ray diffraction peaks up to $2\theta = 110^\circ$. The lattice constant is almost independent of Ni concentration for $x < 0.2$, gradually decreases with increasing Ni concentration

beyond $x=0.2$, where it is about 0.4% larger than those of the bulk Fe–Ni alloys⁽⁹⁾⁽¹⁰⁾. The lattice constant of the *fcc* phase with $x \approx 0.4$ is nearly equal to that of the bulk Fe–Ni alloy with the same Ni concentration⁽⁸⁾. However, it is larger than those of the bulk Fe–Ni alloys for $0.45 < x < 0.6$. The observed lattice expansion is probably related to a loosely packed structure produced by an incorporation of Ar atoms in sputtered films⁽¹¹⁾⁽¹²⁾.

The magnetic moment of the $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys is plotted against alloy concentration, x , in Fig. 3. For all of the $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys, the magnetic moments at 290 K are about 9×10^{-25} J T/atom ($0.1 \mu_B$ /atom) smaller than those at 77 K, indicating their relatively high Curie temperatures. The magnetic moment increases with increasing x for $x < 0.15$ and then decreases monotonically through the *bcc-fcc* phase boundary region. Since the observed magnetic moments at 77 K are nearly equal to those at 0 K, the concentration dependence of the $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys roughly follows the Slater-Pauling curve for $0 < x < 0.6$ ⁽¹³⁾. In bulk Fe–Ni alloys and Fe–Ni alloy films obtained by thermal evaporation and electrodeposition, the concentration dependence of the magnetic moments shows a considerable discontinuity around the *bcc-fcc* phase boundary region⁽²⁾⁽⁴⁾⁽¹³⁾. However, such

a discontinuity could not be detected in the present $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys within the experimental error.

Figure 4 shows the Mössbauer spectra at 77 K for the $\text{Fe}_{1-x}\text{Ni}_x$ alloy films. Only ferromagnetic six line spectra are observed for all of the present alloy films. The linewidth is about 0.28 mm/s for $x=0$ and it increases with increasing x . This line broadening is mainly ascribed to a distribution of hyperfine fields caused by a random atomic arrangement in the neighboring atomic sites of the central ^{57}Fe atom. Here, the spectra could not be decomposed into the spectrum components of the *bcc* and *fcc* phases for the *bcc-fcc* mixed alloys, probably because these two phases show roughly the same hyperfine field. In the Mössbauer spectra of the bulk Fe–Ni alloys with Ni less than 32 at% and fine powdered Fe–Ni alloys^{(14)–(16)}, a single line has been observed at the central position together with the ferromagnetic six lines. This singlet is ascribed to a paramagnetic or an antiferromagnetic state of the *fcc* phase with low Ni concentrations, whose hyperfine field is quite small even at low temperatures. In the present $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys, on the other hand, such a low hyperfine field component could not be observed. On the analysis of hyperfine field distribution as described in the previous paper⁽⁷⁾, the average

Fig. 3 Magnetic moment versus Ni concentration, x , for the $\text{Fe}_{1-x}\text{Ni}_x$ alloys. ● and ○ the present sputtered alloys at 77 K and 290 K, respectively. △: the bulk alloys at 4.2 K⁽¹³⁾. The dash-dot line indicates the Slater-Pauling curve.

Fig. 4 Mössbauer spectra of the sputtered $\text{Fe}_{1-x}\text{Ni}_x$ alloys at 77 K.

Fig. 5 Concentration dependence of average hyperfine field, $\bar{H}_{\text{hf}}$, for the $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys at 77 K (○). The broken line indicates the concentration dependence of magnetic moments for the present $\text{Fe}_{1-x}\text{Ni}_x$ sputtered alloys at 77 K (see Fig. 3).

hyperfine field, $\bar{H}_{\text{hf}}$, was estimated. As shown in Fig. 5, $\bar{H}_{\text{hf}}$ is almost independent of Ni concentration, in contrast to the concentration dependence of average magnetic moment. This indicates that the atomic magnetic moment of Fe atoms is insensitive to the surrounding configuration of Ni atoms.

Since in the Fe-Ni sputtered alloys the magnetic moments and the Mössbauer spectra of the *bcc* phase are almost the same as those

of the *fcc* phase in the *bcc-fcc* phase boundary region, we cannot determine the volume fraction of the *bcc* and the *fcc* phase from these results.

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REFERENCES

- (1) M. Hansen and K. Anderko: *Constitution of Binary Alloys*, McGraw-Hill, (1958), p. 677.
 - (2) C. A. Bauer and P. E. Wigen: *Phys. Rev.*, **B5** (1972), 4516.
 - (3) T. Suzuki and C. H. Wilts: *J. Appl. Phys.*, **38** (1967), 1356.
 - (4) Y. Ueda and M. Takahashi: *J. Phys. Soc. Japan*, **49** (1980), 477.
 - (5) Y. Inokuti and B. Cantor: *Scripta Metall.*, **10** (1976), 655.
 - (6) S. Kachi and H. Asano: *J. Phys. Soc. Japan*, **27** (1969), 536.
 - (7) K. Sumiyama, M. Kadono and Y. Nakamura: *Trans. JIM*, **22** (1981), 686.
 - (8) K. Sumiyama and Y. Nakamura: *Proc. 4th Int. Conf. on Rapidly Quenched Metals*, Japan Inst. Metals, (1982), p. 1549.
 - (9) R. P. Reed and R. E. Schramm: *J. Appl. Phys.*, **40** (1969), 3453.
 - (10) W. B. Pearson: *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, (1958), p. 638.
 - (11) K. Sumiyama and Y. Nakamura: *Trans. JIM*, **23** (1982), 108.
 - (12) K. Sumiyama and Y. Nakamura: *Trans. JIM*, **23** (1982), 595.
 - (13) J. Crangle and G. C. Hallam: *Proc. Roy. Soc. (London)*, **A272** (1963), 119.
 - (14) Y. Nakamura, M. Shiga and N. Shikazono: *J. Phys. Soc. Japan*, **19** (1964), 1177.
 - (15) H. Rechenberg, L. Billard, A. Chamberod and M. Natta: *J. Phys. Chem. Solids*, **34** (1973), 1251.
 - (16) G. N. Belozerskii, V. N. Gittsovich, V. N. Kramer, O. G. Sokolov and Yu. P. Khimich: *Soviet Physics-Solid State*, **13** (1971) 453.
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