Effect of Ar Gas Pressure on Morphology and Structure of Nonequilibrium Fe–Cu Alloys Produced by rf Sputtering

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Fe₁₋ₓCux alloy films sputter-deposited on water-cooled substrates under Ar gas pressures, \( P_{Ar} = 8.9 \) and 0.23 Pa, were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction measurements. The SEM and TEM studies show that the alloy films made under \( P_{Ar} = 8.9 \) Pa have a columnar structure with a grain size of about 20 nm, while those made under \( P_{Ar} = 0.23 \) Pa have a fibrous structure with a grain size of about 10 nm. The primary solid solutions of both bcc and fcc phases are extended in the Fe-rich and Cu-rich regions, respectively in contrast to no solid solution in the equilibrium phase diagram. In the Fe₁₋ₓCux alloys made under a high \( P_{Ar} \), moreover, the single phase regions more widely extend and the oxide phase, CuFeO₂, coexists.

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I. Introduction

Energizing and quenching of materials are a general procedure for producing nonequilibrium phases(1)(2). The sputter-deposition, which is a typical vapor quenching method, gives a variety of chemically homogeneous nonequilibrium alloys(3). Wide ranges of nonequilibrium primary solid solutions have been obtained in Fe₁₋ₓCux alloys sputter-deposited on water-cooled substrates(4): single bcc and fcc phases in the Fe-rich region and the Cu-rich region, respectively, although Fe forms almost no equilibrium solid solution with Cu at room temperature(5). The sputter-deposited Fe₁₋ₓCux alloys with \( x < 0.92 \) are ferromagnetic at low temperatures(6) and Mössbauer spectroscopy of the bcc alloys indicates a tendency of perpendicular magnetic anisotropy near the phase boundary region(6).

During a sputter-deposition process, metal atoms sputtered out of a target strike on a substrate, transfer their kinetic energies to the substrate and become loosely bound adatoms(7). These adatoms diffuse over the surface, exchanging their energies with the substrate and other adsorbed species, until they are either desorbed by evaporation or sputtering or more commonly trapped at low energy lattice sites. The incorporated atoms readjust their positions within the lattice by bulk diffusion. The morphology, microstructure and forming ability of nonequilibrium phases are influenced by several parameters of the sputter-deposition process(7)-(9). Especially, the Ar gas pressure during sputter-deposition, \( P_{Ar} \), determines the structure and morphology of deposited alloy films(10)(11), because Ar atoms collide with sputtered atoms between the target and substrate and affect the energies of metal atoms striking on the substrate.

Sputter-deposited Fe₁₋ₓCux alloy films are candidates for a magnetic recording material and a soft magnetic material(12). Since their magnetic characteristics are strongly correlated with their morphology and structure(10)(13), we sputter-deposited Fe₁₋ₓCux alloys on water-cooled substrates under \( P_{Ar} = 8.9 \) Pa (67 mTorr) and \( P_{Ar} = 0.23 \) Pa(1.7 mTorr). This
paper deals with the experimental results of scanning electron micrograph (SEM), transmission electron micrograph (TEM) and X-ray diffraction measurements. Some experimental results of Fe\textsubscript{1-x}Cu\textsubscript{x} alloys sputter-deposited under \(P_{Ar} = 0.53\) Pa are also described for comparison\cite{460}.

II. Experimental

Using a conventional rf sputtering equipment (sputter up configuration) and composite type targets, about 2 \(\mu\)m thick Fe\textsubscript{1-x}Cu\textsubscript{x} alloy films were deposited on polyimide film and acetylcellulose film substrates. About 80 nm thin alloy films for TEM observation were prepared on rock salt substrates. These substrates were indirectly cooled by water. The operational parameters are listed on Table 1. Ar gas pressure during the sputtering process, \(P_{Ar}\) was kept constant by adjusting a main valve of a diffusion pump and a needle valve for Ar gas. Due to limitation of the pumping power, the main valve was stopped down at \(P_{Ar} = 8.9\) Pa in comparison with the case at \(P_{Ar} = 0.23\) Pa and the effective back ground pressure increases with increasing \(P_{Ar}\). In order to get the alloy films with a similar thickness, a much longer deposition time was required under \(P_{Ar} = 8.9\) Pa than under \(P_{Ar} = 0.23\) Pa. The chemical composition of thick alloy films was determined by electron probe microanalysis (EPMA). Since the chemical analysis was difficult for thin alloy films, we assumed that the composition of thin alloy films was the same as that of thick alloy films made under the same sputtering conditions. The morphology and microstructure of sputter-deposited alloy films were observed by a scanning electron microscope and a transmission electron microscope. The X-ray diffraction pattern was measured using Fe-K\(\alpha\) radiation and a carbon monochromater.

III. Results

Figure 1 shows the scanning electron micrographs of Fe\textsubscript{1-x}Cu\textsubscript{x} alloys sputter-deposited under \(P_{Ar} = 8.9\) and 0.23 Pa. The alloy films made under \(P_{Ar} = 8.9\) Pa have rough surfaces, where columnar grains normal to the film plane are separated by open boundaries: the width of these columns is about 100 nm and that of the boundaries about 10 nm. This structure called Zone 1 has been obtained under sputtering conditions of a high \(P_{Ar}\) and a low substrate temperature\cite{7}. The alloy films sputter-deposited under \(P_{Ar} = 0.23\) Pa, on the other hand, consist of fibrous grains with a flat surface and dense boundaries. This structure called Zone T has been obtained under sputtering conditions of a low \(P_{Ar}\), a high substrate temperature and a negative substrate bias voltage\cite{7-9}. Figure 2 shows the Ar gas pressure-concentration (\(P_{Ar} - x\)) map of the morphology in the sputter-deposited Fe\textsubscript{1-x}Cu\textsubscript{x} alloys. Zone 1 is favorable for the Fe-rich concentration under high \(P_{Ar}\), while Zone T for all over the concentration under low \(P_{Ar}\).

Figure 3 shows the electron micrographs and diffraction patterns of the Fe\textsubscript{1-x}Cu\textsubscript{x} alloys sputter-deposited under \(P_{Ar} = 8.9\) Pa, while Fig. 4 shows those of the alloys sputter-deposited under \(P_{Ar} = 0.23\) Pa. In the alloys made under \(P_{Ar} = 8.9\) Pa, we observed faceted crystallites in the Fe-rich region and round crystallites in the Cu-rich region. The apparent crystal grain size is about 20 nm, but these grains may be a stack of smaller size crystallites normal to the film plane because many reflection fringes are observed in the electron micrograph. In the alloys made under \(P_{Ar} = 0.23\) Pa, small crystallites are observed and the crystal grain

| Back ground pressure during sputtering | \(< 0.11\) mPa (0.8 \(\mu\)Torr) |
|--------------------------------------|---------------------------------|
| for \(P_{Ar} = 8.9\) Pa              | 2.7 mPa (20 \(\mu\)Torr)        |
| for \(P_{Ar} = 0.23\) Pa            | 0.2 mPa (1.5 \(\mu\)Torr)       |
| Ar gas pressure, \(P_{Ar}\)          | \(8.9\) Pa (67 mTorr)           |
|                                       | 0.23 Pa (1.7 mTorr)             |
| Input rf power                       | 150 W                           |
| Target-substrate voltage             | 1.8 kV for \(P_{Ar} = 8.9\) Pa  |
|                                       | 2.2 kV for \(P_{Ar} = 0.23\) Pa |
| Target-substrate distance            | 85 mm                           |
| (during sputter-deposition)          | 350 K                            |
| Deposition rate                       | 0.05 nm/s for \(P_{Ar} = 8.9\) Pa|
|                                       | 0.1 nm/s for \(P_{Ar} = 0.23\) Pa|
size is about 5 nm for the bcc phase and 5-10 nm for the fcc phase. In the electron diffraction patterns, the bcc diffraction rings are observed for the Fe-rich alloys and the fcc ones for the Cu-rich alloys. In the alloys made under \( P_{\text{Ar}} = 8.9 \) Pa, moreover, some diffraction rings can be detected together with the bcc and fcc diffraction rings, being ascribed to the delafossite, \( \text{CuFeO}_2 \)\(^{13}\). The presence of \( \text{CuFeO}_2 \) has been confirmed by analyses of quadrupole splitting and isomer shift of the Mössbauer spectra for the \( \text{Fe}_{1-x}\text{Cu}_x \) alloys made under \( P_{\text{Ar}} = 8.9 \) Pa\(^{14}\).

Figures 5 and 6 show the X-ray diffraction patterns of \( \text{Fe}_{1-x}\text{Cu}_x \) alloy films sputter-deposited under \( P_{\text{Ar}} = 8.9 \) and 0.23 Pa, respectively. In accordance with the previous experiments\(^{10}\), a single bcc phase appears in the Fe-rich concentration region and a single fcc phase in the Cu-rich concentration region. In
the alloys made under $P_{\text{Ar}} = 8.9$ Pa, the signal to noise ratio of diffraction lines is rather poor and a preferred grain growth is not remarkable. A small extra peak is detected around $2\theta = 42^\circ$ and its lattice spacing is about 0.25 nm, being consistent with the electron diffraction measurements. In the alloys made under $P_{\text{Ar}} = 0.23$ Pa, on the other hand, the line intensities of the (110) plane in the bcc phase and the (111) plane in the fcc phase are strong and those of the higher index lines are weak due to the preferred orientation of crystal growth in which the most densely packed planes are parallel to the film planes. The diffraction lines of the alloys made under $P_{\text{Ar}} = 8.9$ Pa are weaker than those of the alloys made under $P_{\text{Ar}} = 0.23$ Pa, indicating that the atomic stacking becomes imperfect with increasing $P_{\text{Ar}}$\(^{(7)}\). The halfwidth of diffraction lines is broadened due to Ar contamination, lattice defects, residual strain and a small grain size in the sputter-deposited alloys. If the line broadening is ascribed completely to the grain size, the average grain sizes are about 10–20 nm, being in agreement with those estimated from the transmission electron micrograph.

Figure 7 shows the lattice constants of Fe\(_{1-x}\)Cu\(_x\) alloys sputter-deposited under several values of $P_{\text{Ar}}$. Since the atomic radius of Fe is almost the same as that of Cu\(^{(15)}\), the lattice constant is rather insensitive to the alloy concentration\(^{(5)}\). With increasing $x$, however, the lattice constant slightly increases in the bcc alloys, while it slightly decreases in the fcc alloys. Moreover, the lattice constant of Fe\(_{1-x}\)Cu\(_x\) alloys made under $P_{\text{Ar}} = 0.23$ Pa is larger than those made under $P_{\text{Ar}} = 8.9$ Pa. The expansion of lattice constant in the alloys made under a low $P_{\text{Ar}}$ may be ascribed to an incorporation of Ar atoms\(^{(16)}\) and an introduction of many interstitial atoms caused by a peening effect\(^{(9)(17)}\).
Fig. 5 X-ray diffraction patterns of Fe$_{1-x}$Cu$_x$ alloys sputter-deposited on water-cooled substrates under Ar gas pressure during sputter-deposition, $P_{Ar}=8.9$ Pa.

Fig. 6 X-ray diffraction patterns of Fe$_{1-x}$Cu$_x$ alloys sputter-deposited on water-cooled substrates under Ar gas pressure during sputter-deposition, $P_{Ar}=0.23$ Pa.

Fig. 7 Lattice constants of Fe$_{1-x}$Cu$_x$ alloys sputter-deposited on water-cooled substrates. The closed circles indicate the results of the alloys made under Ar gas pressure, $P_{Ar}=8.9$ Pa, the open squares those of the alloys made under $P_{Ar}=0.53$ Pa$^4$ and the closed triangles those of the alloys made under $P_{Ar}=0.23$ Pa.
IV. Discussion

1. Morphology and microstructure

Within the present sputtering conditions, monovalent argon ions, \( \text{Ar}^+ \), are mainly produced by rf plasma excitations\(^{(18)}\). They are accelerated in a plasma sheath region near a target and collide with the target. Single metal atoms are sputtered out of the target with receiving the momentum from \( \text{Ar}^+ \)\(^{(9)}\)(\(^{(19)}\)), collide with Ar atoms before they strike on the substrate. Provided that the monoatomic elastic collision is dominant and an excitation and ionization of metal atoms are neglected, the collision process can be estimated in the same way as in the thermalization process of neutrons\(^{(20)}\)-(\(^{(22)}\)). The average energy of sputtered neutral metal atoms, \( E \), is expressed by

\[
E = (E_0 - k_BT_G) \exp \left(-LP_{Ar}\pi d^2/2\right) / k_BT_G,
\]

where \( E_0 \) is the initial energy of metal atoms sputtered from the target, \( k_B \) the Boltzmann constant, \( T_G \) the temperature of surrounding Ar gas atoms, \( L \) the flight length of sputtered metal atoms and \( d \) the scattering parameter which is a sum of Goldschmidt's radii of metal and Ar atoms. The decreasing rate of energy at one collision process, \( \xi \), is written by

\[
\xi = 1 - \frac{(M-1)^2}{2M} \ln \left| \frac{M+1}{M-1} \right|,
\]

where \( M \) is the mass ratio of the target metal atom to the Ar atom. Figure 8 shows the \( E \) versus \( L \) curves for Fe-Ar and Cu-Ar collisions under \( P_{Ar} = 8.9, 0.53 \) and \( 0.23 \) Pa, where we assume \( E_0 = 13 \) eV\(^{(9)}\)(\(^{(21)}\)) and \( T_G = 400 \) K and use the published data on \( d \) and \( M \) in the eqs. (1) and (2)\(^{(15)}\)(\(^{(21)}\)-(\(^{(23)}\)). In the present sputtering equipment, the target-substrate distance is 85 mm. Under \( P_{Ar} = 8.9 \) Pa, sputtered Fe and Cu atoms many times collide with Ar atoms and their average energy at the substrate becomes comparable to the thermal energy of surrounding Ar gas atoms. Under \( P_{Ar} = 0.23 \) and \( 0.53 \) Pa, on the other hand, their average energy is rather high because of a small number of collisions with Ar atoms. Therefore, the probability of metal atoms arriving at the substrate decreases with increasing \( P_{Ar} \), leading to a low deposition rate.

Since the kinetic energy of metal atoms is markedly reduced under a high \( P_{Ar} \), and the surface diffusion of adatoms is insufficient, solid phase nuclei formed at restricted sites on the substrate may grow in their height and width until they come across each other. Then, the incident angle of thermalized metal atoms is randomized so that the steepled points of the growing surface receives more incident flux (shadowing effect), leading to a low atomic density in the grain boundary regions and a random crystal growth (Zone 1)\(^{(7)}\). On the other hand, the kinetic energy of metal atoms are not markedly reduced under a low \( P_{Ar} \), where the surface diffusion of adatoms is enhanced and their momentum component normal to the substrate surface becomes large enough to overcome the shadowing effect and redistributes...
adatoms into valleys. Moreover, since the substrate voltage becomes negative to the plasma potential under a low \( P_{Ar} \) (self bias), bombardments of Ar ions and high energy metal atoms create many nucleation sites for the arriving atoms, or they resputter adatoms. Then we have fine grains, smooth boundary regions and a preferred grain growth (Zone T)(7).

2. Formation of nonequilibrium phases and oxide

On the basis of X-ray diffraction measurements, we estimated the nonequilibrium solubility diagrams of \( \text{Fe}_{1-x}\text{Cu}_x \) alloys sputter-deposited under several values of \( P_{Ar} \), as shown in Fig. 9. In accordance with the previous study(4), the single bcc phase appears in the Fe-rich region and the single fcc phase in the Cu-rich region.

Since the adatoms remain around the struck points of the cold substrate, a highly disordered structure is realized by vapor quenching. Such a disordered structure is usually characteristics of a high temperature phase with a large entropy and a more open and random structure(7). Figure 10 shows the free energy, \( \Delta G \), versus Cu concentration, \( x \), diagrams of \( \text{Fe}_{1-x}\text{Cu}_x \) alloys at several temperatures(24), where the intersection of \( \Delta G \) of the two curves of the bcc and fcc phases shifts to the Fe-rich side with the increase in temperature. Assuming that the nonequilibrium bcc and fcc phases in the sputter-deposited \( \text{Fe}_{1-x}\text{Cu}_x \) alloys reflect the hierarchy of \( \Delta G \) in Fig. 10(25), we have the nonequilibrium phase boundaries shown in Fig. 9 roughly at about 700 K.

The surface diffusion of adatoms is reduced under a high \( P_{Ar} \), while adatoms move on the substrate under a low \( P_{Ar} \) and an initial high temperature phase may be transformed to another metastable phase in accordance with

![Diagram](image)

Fig. 9 Nonequilibrium solubility diagrams of \( \text{Fe}_{1-x}\text{Cu}_x \) alloys sputter-deposited on water-cooled substrates. (a) \( P_{Ar} = 8.9 \) Pa, (b) \( P_{Ar} = 0.53 \) Pa(4) and (c) \( P_{Ar} = 0.23 \) Pa.

![Diagram](image)

Fig. 10 Free energy, \( \Delta G \), of \( \text{Fe}_{1-x}\text{Cu}_x \) alloys. (a) at 900 K, (b) at 700 K, (c) at 500 K and (d) at 300 K(24).
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Ostwald's step rule\(^{(1)(2)(7)}\), leading to a variation of the nonequilibrium solubility diagrams as shown in Fig. 9: the single phase regions of bcc and fcc are slightly wider in the alloys made under \(P_{\text{Ar}}=8.9\) Pa than in those made under \(P_{\text{Ar}}=0.23\) Pa. Comparing the \(\Delta G-x\) diagram of Fe\(_{1-x}\)Ag\(_x\) with that of Fe\(_{1-x}\)Cu\(_x\) alloy\(^{(24)(26)}\), the gradient, \(d(\Delta G)/dx\), at the intersection of the bcc and fcc phases is smaller and the driving force of phase changes is much less for the Fe\(_{1-x}\)Cu\(_x\) alloys than for Fe\(_{1-x}\)Ag\(_x\) alloys. Therefore, the nonequilibrium phase boundary is less sensitive to \(P_{\text{Ar}}\), in the sputter-deposited Fe\(_{1-x}\)Cu\(_x\) alloys than that in Fe\(_{1-x}\)Ag\(_x\) alloys\(^{(11)}\).

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REFERENCES

(1) D. Turnbull: Metall. Trans., 12A (1981), 695.
(2) P. H. Shingu and K. Ishihara: Bull. Japan Inst. Metals, 25 (1986), 16.
(3) K. Sumiyama: Bull Japan Inst. Metals, 25 (1986), 615.
(4) K. Sumiyama, T. Yoshitake and Y. Nakamura: J. Phys. Soc. Japan, 53 (1984), 3160.
(5) O. Kubaschewski: *Iron-Binary Phase Diagrams*, Springer-Verlag, Berlin, (1982), p. 3 and p. 35.
(6) K. Sumiyama, T. Yoshitake and Y. Nakamura: Trans. Japan Inst. Metals, 26 (1985), 217.
(7) J. A. Thornton: *Ann. Rev. Mater. Sci.*, 7 (1977), 239.
(8) J. L. Vossen and J. J. Cuomo: *Thin Film Processes*, ed. by J. L. Vossen and W. Kern, Academic Press, New York, (1978), p. 11.
(9) A. Kimbara: *Sputtering Phenomena*, Tokyo University Press, Tokyo, (1984).
(10) K. Sumiyama, N. Kataoka, K. Takemura and Y. Nakamura: IEEE Trans. Mag., MAG-23 (1987), 3593.
(11) K. Sumiyama, N. Kataoka and Y. Nakamura: Japan J. Appl. Phys., 27 (1988), 1493.
(12) M. Takao and H. Senno: J. Magn. & Magn. Mater., 21-290 and 34-425.
(13) *Powder Diffraction File—JCPDS*, International Centre for Diffraction Data, Philadelphia (1987), 12-752, 21-970.
(14) K. Sumiyama, K. Takemura, N. Kataoka and Y. Nakamura: submitted to Japan J. Appl. Phys.
(15) L. S. Darken and R. W. Gurry: *Physical Chemistry of Metals*, McGraw-Hill, New York, (1953), p. 50.
(16) K. Sumiyama and Y. Nakamura: Trans Japan Inst. Metals, 23 (1982), 198.
(17) T. Kaneko, S. K. Gong and O. Nittorno: Trans. Japan Inst. Metals, 27 (1986), 241.
(18) F. Shinoki and A. Itoh: OYO BUTSURI, 44 (1975), 629.
(19) R. V. Stuart, G. K. Wehner and G. S. Anderson: J. Appl. Phys., 40 (1969), 803.
(20) F. J. Cadieu and N. Chencinski: IEEE Trans. Mag., MAG-11 (1975), 227.
(21) W. D. Westwood: J. Vac. Sci. Tech., 15 (1978), 1.
(22) Y. Hoshi, M. Naoe and S. Yamanaka: Trans. Inst. Electr. Inf. Commun. Eng., J65-C (1982), 921.
(23) *Handbook of Chemistry and Physics*, 55th Edition, ed. by R. C. Weast, The Chemical Rubber Co., (1974-1975), p. B-248.
(24) O. Kubaschewski, J. F. Smith and D. M. Bailey: Z. Metallik., 68 (1977), 495.
(25) N. Saunders and A. P. Miodownik: CALPHAD, 9 (1985), 283.
(26) L. J. Swartzendruber: Bull. Alloy Phase Diagrams, 5 (1984), 560.