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Determination of Cu site in L1₀-FePtCu alloy using ALCHEMI method

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The Cu site in L1₀-ordered ternary FePtCu alloy was quantitatively determined using atom location by channeling enhanced microanalysis (ALCHEMI). The lattice parameter measured by XRD result was $a = 0.388 \pm 0.0003$ nm and $c = 0.369 \pm 0.0009$ nm with an axial ratio c/a of 0.951 ± 0.0003 for ternary L1₀-ordered FePtCu phase. The alloy composition of bulk ternary L1₀-ordered FePtCu phase was Fe₄₀Pt_{50.4}Cu_{9.6} measured by inductively coupled plasma atomic emission spectrometer (ICP-AES). The ALCHEMI result obtained from calculation of the characteristic X-ray spectra demonstrates Cu almost occupies the Fe site in ternary L1₀-ordered FePtCu alloy.

Key words: L1₀-structure, Cu site, FePtCu alloy, ALCHEMI.

Introduction

Recently, much attention has been paid to $L1_0$ -type ordered structure as promising candidates for future ultra-high density magnetic recording media due to its high magnetocrystalline anisotropy constant (K_u) [1]. Since the large K_u values of $L1_0$ -FePt alloys are originated from their tetragonal ordered structures, it is necessary to evaluate the degree of atomic order of those structures when the hard magnetic properties are discussed. For hard magnetic FePt thin continuous films, several reports have been presented on the longrange order (LRO) parameters (S) [2], where S values were determined by using the integrated intensities obtained from x-ray diffraction based on the kinematical scattering theory [3].

A relation of a gradual increase of K_u with S has been reported by two research groups for L1₀-FePt films [4, 5]. However, for small isolated L1₀-nanoparticles, detailed studies of S and the K_u relation have not been performed so far. Additionally, it is very difficult to achieve the equilibrium state of small size particle having high long range order, due to the slow kinetics at low temperature [6]. In order to decrease the atomic ordering temperature, Cu additions have paid much attention for enhancing the transformation kinetics [7]. Barmak et al. reported that phase transformation from A1 to L1₀ in nanoparticles is highly dependent on kinetics such as the nucleation of the L1₀-phase in the successive research of FePt and FePtCu film [8].

It is necessary to compare quantitatively the LRO parameter of L1₀-FePt and FePtCu nanoparticles to study

the Cu effect on L1₀-phase. Sato et al. have reported a method to determine the LRO parameter (S) as a function of particle size via studying the relationship between K_n and the LRO parameter [9]. They showed that LRO parameter (S) of individual single nanoparticles can be estimated precisely by a quantitative electron diffraction analysis which largely simplified the multiple scattering events among the transmitted and diffracted waves, and the multi-slice calculation considering the multiple scattering of electrons. So, it is also important to determine the Cu site in ternary L1₀-FePtCu phase for the basis of electron diffraction analysis and involved LRO parameter S simulation for a study of additive Cu effect on LRO parameter of L10-FePt nanoparticles. However, there is no report on the exact Cu-site in FePt alloy with small amount of additive Cu based on the experiment using diffraction techniques, while replacement of Fe-site by Cu was studied by ultraviolet photoemission spectroscopy and electronic structure calculation [10].

ALCHEMI (Atom Location by Channelling Enhanced Microanalysis [11]) method using the planar channeling does not require complicated calculation of the intensity distribution of incident electrons in a crystal, and can be easily applied to this Cu added $L1_0$ -FePt structure which is alternatively composed of stacking planes of Fe (001) and Pt (001) along the (001) direction. In this paper, Crystallographic site occupancy of additive Cu in ternary $L1_0$ -FePtCu phase was determined using ALCHEMI method.

Experimental

FePt and FePtCu nanoparticles were fabricated by the co-deposition of Fe (99.97%), Pt (99.99%), and Cu (99.96%) targets using rf magnetron sputtering onto NaCl substrate cleaved in air. The sputtering was performed in Ar (99.999%) gas at a pressure of 1.33 Pa and a power of 30 W with a chamber base pressure of

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 5×10^{-6} Pa. Particle size and particle density were controlled by changing the sputtering duration between 40 and 150 sec and substrate temperatures between 563 and 613 K. Annealing of the specimen was not performed after the deposition. After the sputtering, exsitu deposition of amorphous Al₂O₃ and carbon film was performed at room temperature to coat the nanoparticles. The specimen films were mounted on Mo grids for TEM observation after removing the NaCl substrates in distilled water. Structural characterization including NBD was performed by using JEOL JEM-3000F transmission electron microscopes (TEMs) operated at 300 kV. Images and diffraction patterns were digitally recorded by using imaging plates (IPs, Fuji Film FDL-UR-V) for later quantitative intensity analysis. Alloy compositions were analyzed by energydispersive x-ray spectrometer (EDS) attached to 300 kV TEM.

XRD measurements were carried out on a Philips X'pert x-ray diffractometer with a four-circle goniometer using Co K α radiation (x-ray wavelength of $\lambda = 0.1789$ nm) at 45 keV and 40 mA. The chemical composition of FePtCu alloy was measured by inductively coupled plasma atomic emission spectrometer (ICP-AES). The ALCHEMI analysis was performed using JEOL JEM-3000F trans-mission electron microscopes (TEMs) under the 200 kV and the EDS spectrum was also obtained from equipped system.

In order to find out optimum diffraction conditions, we measured the X-ray spectra several times as a slight deviation around the exact Bragg condition changed. The EDS spectra around a superlattice reflection are very sensitive considering the convergent angle about 30 mrad from the diameter of the reflections. In the two different conditions of s > 0 and s < 0 and same selected area, we measured X-ray intensities several times when Fe or Pt peaks were significantly excited, because the density distribution of the incident beam

electrons in the parallel to the Fe or Pt planes shows the significant variation of X-ray intensity. The EDS spectra on the two diffraction conditions was measured until X-ray intensities were stabilized and obtained enough to ignore the experimental error due to the counting statistics. Generally, because the experimental error of counting statistics is proportional to $1/(N^{1/2})$, we obtained EDS spectra more than ten thousands counts in ternary elements respectively, which shows the 99.0% confidence level. In order to determine accurately, we also measured EDS intensities from different crystal and the experimental error which follows above method was less than 1.0%. This experiment was repeated a few times for the reproducibility of this quantification process.

Results and Discussion

The low temperature atomic ordering of L10-FePt nanoparticle was promoted by co-deposition of Cu as low as 613 K. The degree of atomic ordering toward L1₀-ordered phase was considered as a function of the particles size, which can be controlled by sputtering duration. As the sputtering duration are prolonged from 40 to 150 sec, different tendencies are found in nanostructure evolution between binary L10-FePt and ternary L10-FePtCu alloys even under a same sputtering condition. Figure 1 shows bright-field (BF) TEM images and corresponding selected area electron diffraction (SAED) patterns for ternary (Figs. 1(a-d)) and binary (Figs. 1(e-h)) alloy nanoparticles formed at 613 K varied from 40 to 150 sec. The ternary alloy nanoparticles showed densely-dispersed and isolated island-like nanoparticles on the substrate surface in (a) 40 and (b) 60 sec. But in the prolonged sputtering duration at (c) 120 and (d) 150 sec, the coalescence and sintered growth occurred significantly.

The formation of strongly <100> oriented FePtCu



Fig. 1. Bright field TEM images and corresponding SAED patterns of FePtCu phase formed at (a) 40 sec, (b) 60 sec, (c) 120 sec and (d) 150 sec, and FePt phase formed at (e) 40 sec, (f) 60 sec, (g) 120 sec and (h) 150 sec.

nanoparticles can be confirmed by the selected area electron diffraction (SAED) pattern. In the SAED pattern, both (001) and (110) superlattice reflections of the $L1_0$ structure are observed, indicating the proceeding of the atomic ordering reaction in the as-deposited condition. No reflections of bcc-Fe or fcc-Cu are observed, indicating the formation of ternary $L1_0$ phase. Basically, disordered FePt is FCC structure which Fe and Pt atoms occupy the FCC site randomly. But L1₀-FePt for high magnetocrystalline anisotropy constant (K_u) is ordered by the thermal treatment at high temperature around 873 K. The high K_u is originated from the L1₀-type tetragonal ordered structure which has the alternative stacking planes of Fe (001) and Pt (001) along the (001) direction. Also, when FePt is ordered to L1₀-structure, these (001) superlattice reflections are occurred, while (001) superlattice reflections in disordered FCC or other phase like BCC Fe and FCC Cu cannot be observed. The ordering temperature of 613 K for L10-FePtCu nanoparticles is 260 K lower than that of the L1₀-FePt nanoparticles fabricated by our electron-beam deposition [12]. The low-synthesis temperature of the $L1_0$ structure at 613 K is as low as those of FePt artificial lattices [13] or Fe/Pt multilayered films [14] fabricated by the alternate stacking of Fe and Pt.

On the other hand, the binary FePt nanoparticles fabricated at 613 K under different sputtering duration showed a different tendency in the morphology and degree of atomic ordering as shown in Fig. 1(e-h). As the sputtering duration increased, the particle size increased due to the particle coalescence, and the superlattice reflections of (001) and (110) appeared in the specimens sputtered in the duration of (e) 40 (f) 60, (g) 120 and (h) 150 sec. But the intensity of these (001) and (110) superlattice reflections is quite weak. The particle areal density becomes much lower than the ternary FePtCu nanoparticles. As the sputtering duration increases, binary L10-FePt nanoparticles show the more coalesced and sintered morphology by surface migration. This indicates that Cu addition affects the growth process of FePt nanoparticles, and as a consequence, it prevents the coalescent growth of islands.

Figure 2 shows the XRD result of ternary L1₀ordered FePtCu specimen sputtered in the duration of 150 sec. The lattice parameter measured by XRD result was $a = 0.388 \pm 0.0003$ nm and $c = 0.369 \pm 0.0009$ nm with an axial ratio c/a of 0.951 ± 0.0003 for ternary L1₀-ordered FePtCu phase. The obtained axial ratio is lower than those of the bulk L1₀-FePt binary phase (c/ a = 0.964 [15]), which indicate that the additive Cu is responsible for reducing the axial ratio of L1₀-ordered FePt phase. Note that a reported axial ratio for a bulk ternary L1₀-FeCuPt₂ compound is quite low as low as 0.923 [16]. The alloy composition of bulk ternary L1₀ordered FePtCu phase was Fe₄₀Pt_{50.4}Cu_{9.6} measured by inductively coupled plasma atomic emission spectrometer



Fig. 2. XRD result of ternary FePtCu alloy sputtered during 150 sec. The measured lattice parameter was $a = 0.388 \pm 0.0003$ nm and $c = 0.369 \pm 0.0009$ nm with an axial ratio c/a of 0.951 ± 0.0003 .



Fig. 3. Two electron diffraction condition of (a) s > 0 and (b) s < 0.

(ICP-AES).

Figure 3 shows the electron diffractions taken by only exciting (001) systematic reflection under the two beam condition, where the atomic planes are alternately arranged. The crystal was tilted to change the deviation parameter s positive and negative along the Kikuchi line movement between the direct beam and the diffraction spot. The diameter of measured area by energy-dispersive x-ray spectrometer was about 350 nm in specimen surface. The (001) and (002) reflection were excited under the two electron diffraction condition of (b) s > 0 and (c) s < 0 respectively.

The two electron diffraction conditions under which the characteristic X-ray spectra were taken are shown in Fig. 4 for the conditions of (a) s > 0 and (b) s < 0, where s > 0 and s < 0 corresponds to the off-Bragg condition with the excitation error (s) inside and



Fig. 4. Corresponding characteristic X-ray spectra normalized by Pt peak intensity under (a) s > 0 and (b) s < 0, respectively. When Fe peak intensity increased under the excitation of (001) plane (s > 0), the Cu peak intensity also increased, which strongly imply the substitution of Cu on Fe site. On the contrary, when the Pt peak intensity increased under the excitation of (002) plane (s < 0), the Cu peak intensity decreased.



Fig. 5. The channeling condition depending on the excitation error (*s*) for the (001) superlattice reflection.

outside the Ewald sphere, respectively. These excitation conditions are illustrated in Fig. 5. In Fig 4(a), when the Fe peak intensity increased under the excitation of (001) plane, the Cu peak intensity also increased, which strongly implies the substitution of Cu on Fe site. On the contrary, when the Pt peak intensity increased under the excitation of the standing wave along the (002) plane, the Cu peak intensity decreased in Fig. 4(b). The characteristic X-ray spectra corresponding to each condition are normalized by Pt peak intensity. The characteristic X-ray intensities, $N_{P_l}^{(n)}$, $N_{F_e}^{(n)}$ and $N_{Cu}^{(n)}$ from Fe, Pt and Cu atoms of Fe_xPt_yCu_z are given as [1],

$$N_{Fe}^{(n)} = P_{Fe} x \psi_a^{(n)} \tag{1}$$

$$N_{P_t}^{(n)} = P_{p_t} \{ (y - \omega) \psi_a^{(n)} + \omega \psi_\beta^{(n)} \}$$
(2)

$$N_{Cu}^{(n)} = P_{Cu} z \{ k \psi_a^{(n)} + (1-k) \psi_{\beta}^{(n)} \}$$
(3)

where ω is the atomic ratio of Pt in the β site, and and are the thickness averaged electron intensities on the α and β planes, respectively. The superscript (n) denotes the diffraction condition of n = 1 for s > 0, n = 2 for s < 0 and n = 3 for non-channeling. The P_{Pt}, P_{Fe} and P_{Cu} are the scaling factors which consider the differences in X-ray fluorescent yields of Pt, Fe and Cu. The first and second terms in Eq. (1) represent the X-ray intensities from Pt

atoms at the α and β sites, respectively, where those in Eq. (3) represent the X-ray intensities from Cu at these two sites. The unknown parameters such as P_{Pt}, P_{Fe}, P_{Cu}, $\psi_{\alpha}^{(n)}$ and $\psi_{\beta}^{(n)}$ can be eliminated from these relation, so, the k, fraction of Cu atom in α plane is easily obtained as follows,

$$k = \frac{N_1 \cdot R^{(1)} - N_2 \cdot R^{(2)}}{N_2 \cdot (1 - R^{(2)}) - N_1 \cdot (1 - R^{(1)})}$$
(4)

$$N_1 = \frac{N_{F_e}^{(1)}}{N_{F_e}^{(2)}}$$
(5)

$$N_2 = \frac{N_{Cu}^{(1)}}{N_{Cu}^{(2)}} \tag{6}$$

and

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$$R^{(n)} = \frac{x}{y} \cdot \frac{N_{Fe}^{(3)}}{N_{Pl}^{(3)}} \cdot \frac{N_{Pl}^{(n)}}{N_{Fe}^{(n)}} - \frac{x - \omega}{\omega}$$
(7)

, where $R^{(n)}$ stands for $\psi_a^{(n)}/\psi_\beta^{(n)}$.

In Eq. (7), ω depends on the *k*, and so, R⁽ⁿ⁾ is still unfixed. To calculate the exact k value, dummy number is inserted into *k* in Eq. (7). After getting *k* from Eq. (4), this value is inserted into Eq. (7) again to obtain *k* more accurately. This procedure is repeated to attain the exact *k* value. The integrated intensities of characteristic X-ray from each channeling condition and the calculated Fe, Pt and Cu composition which occupy α (Fe site) and β (Pt site) sites are shown in Table 1 and 2, respectively. The average ratio of calculated Cu substitution on Fe site was 99.0% which indicates the Cu almost substitute the Fe site. This result is well consistent with other calculation result that Cu occupies the Fe site randomly [10].

Conclusions

In summary, we have quantitatively demonstrated locating atom position of Cu in ternary L1₀-FePtCu

Table 1. Measured characteristic X-ray intensities of ternary bulk

Table 2. Calculated site occupancy of α and β site in ternary bulk Fe₄₀Pt_{50.4}Cu_{9.6} alloy.

13018

13063

14302

	<i>a</i> -site	β -site
Pt (at. %)	0.38	50.02
Fe (at. %)	40.00	0.00
Cu (at. %)	9.49	0.11

alloy by the ALCHEMI experiment technique using the electron diffraction and the characteristic X-ray spectra. The average ratio of substitution of Cu on Fe site in ternary L1₀-FePtCu alloy was more than 99.0%, which indicates the Cu almost substitutes the Fe site. In order to study the Cu effect on L1₀-FePt nanoparticle, this result gives a basis for quantitative analysis of LRO parameter of individual single L1₀-FePt nanoparticles using electron diffraction technique and multi-slice calculation. This technique can also be extended to the locating other additives which make the solid solution with L1₀-FePt phase as like Co without adjusting any parameters such as crystal thickness.

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