Low temperature synthesis of FePt alloy nanoparticles by polyol process

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Abstract. Low temperature synthesis of equiatomic FePt alloy nanoparticles with the FCC structure was carried out by the polyol process in the presence of NaOH at above 383 K. The Pt content in the FePt alloy particles decreased with decreasing reaction temperature and equiatomic FCC-FePt alloy nanoparticles were successfully obtained at 383 K. When the FCC-FePt alloy nanoparticles synthesized at 383 K were annealed at 573 K, a partially ordered phase with the L₁₀ structure was observed. For comparison, FCC-FePt alloy nanoparticles were synthesized at 468 K without adding NaOH. Results showed that the degree of atomic ordering of the sample synthesized at 383 K with the addition of NaOH was higher than those obtained at 468 K after annealing at low temperatures. Thus, it is concluded that the temperature employed during the synthesis of FCC-FePt alloy nanoparticles affects the ordering transformation temperature.

1. Introduction

Equiatomic L₁₀-FePt alloy shows large magnetic anisotropy that depends on the degree of atomic ordering [1]. The control of such degree of equiatomic L₁₀-FePt alloy nanoparticles is important for advanced magnetic recording media applications [2,3].

Liquid phase synthesis of FePt alloys has been actively investigated because well-dispersed equiatomic FePt alloy nanoparticles could be obtained by adjusting the synthesis conditions [2]. For example, thermal decomposition of Fe(CO)₅ and reduction of Pt(C₅H₇O₂)₂ in octyl ether and 1,2-alkanediol are a well-known method to produce FePt alloy nanoparticles [2,3]. Other liquid phase methods that use reducing agents such as polyols [4], hydrazine [5] or borohydride [6] have also been reported. Since disordered FCC-FePt alloy nanoparticles are prepared with these methods, heat treatment is necessary to obtain large magnetic anisotropy [2,3]. However, the heat treatment is carried out at high temperatures, resulting in the agglomeration and particle growth of nanoparticles [7]. Therefore, it is necessary to lower the ordering transformation temperature from the FCC to the L₁₀-type structure to keep the size of the as-synthesized FePt alloy nanoparticles invariable.

There are several reports on the results of lowering the ordering transformation temperature [8-10]. These results show that the ordering transformation temperature of the FCC-FePt alloy nanoparticles can be decreased by adding Ag salts in the synthesis step [8] and also by annealing the FePt particles in high pressure H₂ gas [9]. On the other hand, the ordering transformation temperature of FePt nanoparticles has been found to decrease when a low molar ratio between ethylene glycol (EG) to Pt salts, EG/Pt, is used in their synthesis [4]. It has been proposed that the ordering transformation
The reduction rate of metallic ions decreases with decreasing reaction temperature. In the case of the FePt system, the Pt ions are easily reduced compared to Fe ions, so it is expected that Pt metal can be obtained at lower temperatures than that needed to obtain Fe metal. Therefore, it is necessary to enhance the reduction rate of Fe ions to synthesize equiatomic FePt alloy nanoparticles at low temperatures [12-14]. Recently, metal Fe and FeCo alloy nanoparticles have been synthesized at low temperatures by the polyol process in the presence of hydroxyl ions [11,14]. By the addition of hydroxyl ions, the continuous dehydration of ethylene glycol and formation of acetaldehyde is enhanced resulting in the reduction of metallic ions [14]. Hence, it has been considered that the concentration of hydroxyl ions plays a major role in enhancing the reduction of the metallic ions such as Fe ions [11,14]. In this study, we extended these results in the synthesis of FCC-FePt alloy nanoparticles at relatively low temperatures and furthermore investigated the effect of reaction temperature on the ordering transformation temperature of FePt particles.

2. Experimental

The synthesis of FePt particles was carried out using FeCl$_2$·4H$_2$O and Pt(C$_5$H$_7$O$_2$)$_2$ as precursors. Ethylene glycol was used as solvent and reducing agent, and NaOH was added in order to introduce hydroxyl ions to the reaction solution. Assuming that the reduction rate of Pt ions is higher than that of Fe ions, the initial molar ratio of Fe salts to Pt salts introduced to the polyol solution was set at 7 to 3. Reaction time was 1 h and reaction temperature was set at 373, 383, 403, 423 and 443 K. The crystal phases of precipitated particles were analyzed by X-ray diffractometry (XRD). The morphology and the size of precipitated particles were observed by transmission electron microscopy (TEM). To determine the Pt contents, the precipitated particles were dissolved in aqua regalis and then diluted. The obtained solution was then analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The precipitated equiatomic FCC-FePt alloy nanoparticles were annealed in Ar-5%H$_2$ at 473-1173 K for 1 hr. After heat treatment, XRD measurements were conducted to evaluate the degree of atomic ordering.

3. Results and discussion

The reduction of metal salts was not possible at temperatures below 373 K; successful synthesis of precipitates was possible at reaction temperatures above 383 K. Figure 1(a) shows a TEM image of the precipitated particles synthesized at 383 K. Well-dispersed spherical particles with an average diameter of 2 nm were obtained. It was observed that the particle size of the precipitate increased to

![Figure 1](image-url)
about 5 nm when the reaction temperature was increased to 443 K. It is noted that cubic-shaped Fe particles of several tens of nanometers in size have been synthesized by the NaOH-polyol process at 403 K [11]. However, the shape and size of the precipitated particles obtained in this work, as shown in Fig. 1(a), differed from those of the Fe metal fine particles. In addition, when the synthesis was carried out without NaOH, no particles were obtained at below 403 K. This suggests that not only the reduction of Fe ions but also the reduction of Pt ions is accelerated by hydroxyl ions in polyol solution. Therefore, the precipitated nanoparticles shown in Fig. 1(a) are expected to be FePt alloy.

Figure 1(b) shows the XRD pattern of the precipitated nanoparticles synthesized at 383 K together with reference data of Fe metal with the BCC structure (JCPDS#06-0696), Pt metal with the FCC structure (JCPDS#04-0802) and equiatomic FePt alloy with the FCC structure (JCPDS#29-0718) from the International Centre for Diffraction Data (ICCD) database. The diffraction pattern is assigned to the FCC single phase, and diffraction peaks assigned to the BCC phase are not observed. In addition, since the diffraction pattern of the precipitated nanoparticles is observed at higher angles in comparison with that of Pt metal, the lattice constant of the precipitated nanoparticles is smaller than that of Pt. Accordingly, the precipitated nanoparticles are considered to be FePt alloy with the FCC structure.

The magnetic anisotropy of L1$_0$-FePt alloy depends on the alloy composition [15]. The reaction temperature dependence of the Pt content in FePt alloy nanoparticles is shown in Fig. 2. Although the initial molar ratio of Fe salts to Pt salts was 7 to 3, the Pt content in the FePt alloy nanoparticles synthesized at 443 K was 62 at%. The reduction rate of Pt ions is regarded to be much higher than that of Fe ions at 443 K. The Pt content in FePt alloy nanoparticles decreases with decreasing reaction temperature. As a result, the equiatomic FePt alloy particles are obtained at reaction temperatures below 403 K, suggesting that the reduction rate of Pt ions becomes almost equivalent to that of Fe ions at this temperature. This suggests that the reduction rate of Pt ions has a strong temperature dependence in comparison with that of Fe ions.

Fe$_{51}$Pt$_{49}$ alloy particles with the FCC structure synthesized at 383 K were annealed at different temperatures, $T_a$. The XRD results of these particles are presented in Fig. 3(a) together with reference data of equiatomic FePt alloy with the FCC structure (JCPDS#29-0718) and FePt alloy with the L1$_0$ type structure (JCPDS#43-1359) from the ICCD database. It has been reported that equiatomic FePt alloy nanoparticles are synthesized at relatively high temperatures such as 468 K by the reduction of Fe(C$_5$H$_7$O$_2$)$_3$ and Pt(C$_5$H$_7$O$_2$)$_2$ in ethylene glycol without NaOH [4]. According to this report, the FePt alloy nanoparticles with the FCC structure were synthesized for comparison with the Fe$_{51}$Pt$_{49}$ alloy particles synthesized at 383 K with NaOH. The Pt content of the particles synthesized at 468 K was about 53 %, which was close to that of the particles synthesized at 383 K. Also, the average size of the obtained particles was about 2.5 ± 0.5 nm, which was quite similar to that of the particles synthesized at 383 K. The XRD patterns after annealing the equiatomic FePt alloy nanoparticles synthesized at 468 K without NaOH are shown in Fig. 3(b). The diffraction peak position of (111) for the L1$_0$-FePt alloy is higher than that for the FCC-FePt alloy. This is believed to be due to the
A decrease in the c/a ratio caused by the change in crystal structure from cubic to tetragonal. In Fig. 3(a), the (111) peak position of the FCC structure is slightly shifted to a higher angle in the alloy particles annealed at $T_a = 473$ K. In addition, in the alloy particles annealed at $T_a = 573$ K, peaks assigned as (001) and (110) of $L_1_0$-FePt were observed. These peaks are superlattice lines, suggesting that atomic ordering occurred at $T_a = 573$ K. On the other hand, in the case of FePt alloy nanoparticles synthesized at 468 K without NaOH, diffraction peaks related to atomic ordering were not detected in the alloy particles annealed at $T_a = 573$ K, although the (111) peak was shifted to a higher angle. In these particles, atomic ordering was observed after annealing at $T_a = 673$ K.

To compare the behavior of atomic ordering due to heat treatment in detail, ordering parameter $S$ is evaluated. The value of $S^2$ is calculated by dividing the ratio of integrated peak intensity of (110) to (111), i.e., $I_{(110)}/I_{(111)}$measured by $I_{(110)}/I_{(111)}$ideal for an ideally ordered phase, as shown in Eq. (1).

$$S^2 = \frac{I_{(110)}/I_{(111)}\text{measured}}{I_{(110)}/I_{(111)}\text{ideal}},$$

where the value of $I_{(110)}/I_{(111)}$ideal is estimated theoretically. Figure 4 shows $T_a$ dependence of $S$ for the

![Figure 3](image1.png)

**Figure 3** X-ray diffraction patterns of FCC-FePt alloy nanoparticles synthesized at (a) 383 K with NaOH and (b) 468 K without NaOH before and after heat treatment at $T_a = 473, 573, 673, 773$ and 1173 K.

![Figure 4](image2.png)

**Figure 4** Annealing temperature ($T_a$) dependence of the ordering parameter $S$ of FCC-FePt alloy nanoparticles synthesized at 383 K with NaOH and at 468 K without NaOH.
equiatomic FePt alloy nanoparticles synthesized at 383 K with NaOH and at 468 K without NaOH. Compared with the values of $S$ at a relatively low $T_a$ such as 673 K, the value of $S$ for the FePt alloy nanoparticles synthesized at 383 K is much larger than that for the particles synthesized at 468 K without NaOH. At $T_a = 773$ K or higher, there is a little difference in the value of $S$ for each annealed particle. Consequently, the lower reaction temperature in the synthesis of equiatomic FePt alloy nanoparticles led to the lowering of ordering transformation temperature from the disordered FCC structure to the ordered L1$_0$ type structure.

The ordered phase with the L1$_0$-type structure is thermodynamically stable for equiatomic FePt alloy below about 1573 K. It is believed that the disordered phase with the FCC structure of the particles synthesized at 383 and 468 K in polyol solution is a consequence of fast rate of reduction in synthesis, implying that the slight atomic order is caused by the low reduction rate in synthesis. In other words, small difference in atomic ordering between the particles synthesized at 383 and 468 K are expected, although superlattice line due to the atomic ordering cannot be detected by x-ray measurements as shown in Fig. 3. In addition, the amounts of defects such as vacancy and dislocation for the former are expected to be larger than that for the latter because of low reaction temperature. Note that such defects promote the diffusion of Fe and Pt atoms in particles during heat treatment [10]. The effects mentioned above are speculated to cause the lowering of ordering transformation temperature.

4. Conclusion
Equiatomic FCC-FePt alloy nanoparticles were successfully synthesized at 383 K by the polyol process by adding NaOH. When FCC-Fe$_{51}$Pt$_{49}$ alloy particles were annealed at 573 K, a partially ordered phase with the L1$_0$ structure was observed. Compared to the FePt alloy nanoparticles synthesized at 468 K without the addition of NaOH, the degree of atomic ordering of nanoparticles synthesized at 383 K increased after annealing at low temperatures. In conclusion, the ordering transformation temperature of FCC-FePt alloy nanoparticles is affected by the reaction temperature in synthesis.

5. Acknowledgement
This work was partly supported by a Grant-in-Aid for Young Scientists (B), No. 23760620, from the Japan Society for the Promotion of Science (JSPS).

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