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Transformation to $L1_0$ structure in FePd nanoparticles synthesized by modified polyol process

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Abstract

FePd nanoparticles were prepared by the modified polyol process, i.e. simultaneous reduction of palladium acetylacetonate and thermal decomposition of iron pentacarbonyl in a solvent. The well-dispersed FePd particles, with the average particle size of ~ 8.4 nm, were obtained using diphenyl ether as a solvent. The structure of FePd nanoparticles transformed to $L1_0$ structure from face centered cubic (fcc) structure after annealing at 600 $^\circ$C for 1 h in vacuum. The coercivity of the ordered FePd nanoparticles increased to ~ 2 kOe at 5 K from ~ 0.6 kOe in the fcc as-made FePd nanoparticle. On the other hand, FePd nanoparticles, synthesized based on the conventional modified polyol process using dioctyl ether as a solvent, showed no structural transformation after annealing up to 700 $^\circ$C. This is explained in terms of the interruption of thermal diffusion of Fe and Pd atoms during the thermal treatment due to the mixture of interstitial carbon impurity in the synthesis process using dioctyl ether as a solvent.

Keywords: FePd; Nanoparticles; $L1_0$ structure; Polyol process; Coercivity; Impurity

1. Introduction

$L1_0$-type FePt, CoPt and FePd binary alloys have large uniaxial anisotropy ($\text{FePt}: K_u=6.6–10 \times 10^7 \text{ erg/cm}^3$, $\text{CoPt}: K_u=4.9 \times 10^7 \text{ erg/cm}^3$ and $\text{FePd}: K_u=1.8 \times 10^7 \text{ erg/cm}^3$) [1]. Therefore, the ordered alloys are the attractive materials for future high density recording media. Recently, the synthesis of the ordered alloy nanoparticles, based on chemical techniques, has been actively developed after the epoch-making report on the synthesis method of FePt nanoparticle by Sun et al., in which they showed that the face centered cubic (fcc) as-made FePt nanoparticles, prepared by the simultaneous thermal decomposition of iron pentacarbonyl (Fe(CO)$_5$) and reduction of palladium acetylacetonate (Pd(acac)$_2$), transformed to the $L1_0$ structure after annealing at 600 $^\circ$C [2].

Chen and Nikles, however, showed that the FePd nanoparticles, synthesized by the modified polyol process including the thermal decomposition of iron pentacarbonyl (Fe(CO)$_5$) and reduction of platinum acetylacetonate (Pt(acac)$_2$), transformed to the $L1_0$ structure after annealing at 600 $^\circ$C [2].

Chen and Nikles, however, showed that the FePd nanoparticles, synthesized by the modified polyol process including the thermal decomposition of iron pentacarbonyl (Fe(CO)$_5$) and reduction of palladium acetylacetonate (Pd(acac)$_2$) which is modified from the synthesis process of FePt nanoparticles by Sun et al., did not transform to the $L1_0$ phase even after annealing at a sufficient high temperature (550–700 $^\circ$C) [3]. On the other hand, CoPt nanoparticles, prepared by the simultaneous process of thermal decomposition of cobalt tricarbonyl nitrosyl (Co(CO)$_3$NO) and reduction of Pt(acac)$_2$, transform to $L1_0$ structure after annealing at 700 $^\circ$C [3]. Recently, Kang et al. showed that the FePd nanoparticles, prepared by the simultaneous chemical reduction of iron chloride ($\text{FeCl}_2$·4-$\text{H}_2\text{O}$) and Pd(acac)$_2$, transform to $L1_0$ structure after annealing at 550 $^\circ$C [4]. Thus, the FePd nanoparticles, synthesized by the modified polyol process including the thermal decomposition, does not show the $L1_0$ phase transition after annealing exclusively in the typical $L1_0$ type materials such as FePt, CoPt and FePd, but the FePd nanoparticles, prepared by polyol process composed of only the reduction process, form the $L1_0$ phase. This kind of contrast between FePd and another binary alloys should reflect the intrinsic mechanism for the disordered–ordered phase transition in metallic alloy systems. However, there has not been any information about the origin of difficulty in $L1_0$ transformation of FePd nanoparticles prepared by the modified polyol process, although it is helpful for the development of the ordered metallic alloy nanoparticles synthesized by chemical method.

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According to the recent reports [5], the temperature for L1\textsubscript{0} transformation of FePt nanoparticle drastically changes due to mixture of third element through the change in diffusion rate of Fe and Pt atoms during the thermal treatment. This suggests that the decrease in the diffusion rate of constituent atoms, induced by mixing of some impurities, can cause the difficulty of L1\textsubscript{0} transformation in FePd nanoparticle. Thus, a possible approach to realize the L1\textsubscript{0} transformation in FePd nanoparticles prepared by the synthesis using thermal decomposition of Fe(CO)\textsubscript{5} is to increase the diffusion rate of atoms by decreasing the impurities content.

In this work, we synthesize FePd nanoparticles based on the modified polyol process in which diphenyl ether is used as a solvent in stead of dioctyl ether that has been conventionally used in the modified polyol process. As a result, we observe the L1\textsubscript{0} transformation from the disordered fcc structure in the FePd nanoparticles synthesized using thermal decomposition of Fe(CO)\textsubscript{5}. In addition, we discuss the ordering process of the FePd nanoparticles synthesized by the modified polyol process in terms of the change in diffusion rate of constituent atoms accompanied by the admixture of impurities.

2. Experimental

FePd nanoparticles were synthesized basically based on the modified polyol process. Chen and Nikles [3] used dioctyl ether as a solvent in the synthesis process, which is same as that in the synthesis of FePt nanoparticles reported by Sun et al. [2]. However, we partially modified this method, i.e. diphenyl ether was used as a solvent, because Pd(acac)\textsubscript{2} is easily dissolved in diphenyl ether but not in dioctyl ether. The reductant was 1,2-hexadecanediol and the stabilizer was a combination of oleic acid and oleylamine.

The mixture of Pd(acac)\textsubscript{2} (120–130 mg), 1,2-hexadecanediol (390 mg), diphenyl ether (20 ml), oleic acid (0.16 ml), and oleylamine (0.17 ml) were heated to 100 °C in a flask under N\textsubscript{2} atmosphere. After dissolution of Pd(acac)\textsubscript{2} in diphenyl ether, Fe(CO)\textsubscript{5} (0.10 ml) was quickly injected with syringe to the mixture and well mixed by stirring. The mixture was heated to 259 °C, the boiling temperature of diphenyl ether, and refluxed for 10 min. After the reflux, the mixture was cooled down to room temperature, and then the particles were precipitated by adding ethanol (40 ml) and centrifuging. The resultant FePd nanoparticles were annealed at 600 °C for 1 h in vacuum (6 × 10\textsuperscript{−6} Torr) to accelerate the structural ordering.

The composition of the particles was determined by the electron probe microanalyzer (EPMA). The morphology and the particle size were observed using the transmission electron microscope (TEM). The crystal structure and the lattice constant were determined by the X-ray diffraction (XRD). The magnetic hysteresis of the nanoparticles was obtained using a superconducting quantum interference device (SQUID) magnetometer. In addition, the impurity mixed in the synthesis process of Pd nanoparticle was investigated using X-ray photoelectron spectroscopy (XPS) by investigating the binding energy of Pd.

3. Results and discussion

3.1. Character of FePd nanoparticles synthesized by modified polyol process

Fig. 1 shows the TEM image and size distribution of the as-made FePd nanoparticles. The well-dispersed particles, with the average particle size of ~8.4 nm and the relatively broad distribution of particle size, were obtained. After annealing at 600 °C to accelerate the structural ordering, the coagulation of particles occurred.

Fig. 2 shows the XRD patterns of the as-made Fe\textsubscript{47.1}Pd\textsubscript{52.9} nanoparticles and the Fe\textsubscript{47.1}Pd\textsubscript{52.9} nanoparticles annealed at 600 °C for 1 h in vacuum (6 × 10\textsuperscript{−6} Torr). The as-made FePd nanoparticles have fcc structure (disordered phase). After the annealing at 600 °C, the structure of FePd nanoparticles transformed to L1\textsubscript{0} type (ordered phase). As shown in Fig. 3, the hysteresis loops at 5 K of the Fe\textsubscript{49.2}Pd\textsubscript{50.8} samples with the fcc and L1\textsubscript{0} structures correspond to coercive forces of 630 and
Thus, the increase in coercive force of the FePd nanoparticles, synthesized by the modified polyol process, is induced by the transformation to L10 from fcc structure. As a result, the structural transformation in FePd nanoparticles, prepared by the synthesis using thermal decomposition of Fe(CO)₅, was confirmed based both on the structural and magnetic analysis.

### 3.2. Ordering process of FePd nanoparticles

We discuss the ordering process of the FePd nanoparticles, synthesized by the modified polyol process, and especially the reason why the present nanoparticle sample of FePd showed the structural transformation by annealing in contrast to the previous study [3]. The comparison of the preparation procedure by Chen and Nikles [3] with the present procedure suggests that the difference of solvents used with the reflux relates with the L1₀ transformation. In order to clarify the contribution of solvent to the structural transformation, the Pd nanoparticles were synthesized by the polyol process using the two kinds of solvents, where the dissolubility of Pd(acac)₂ is significantly higher in diphenyl ether than in dioctyl ether.

Fig. 4 shows the XRD patterns of the Pd and FePd nanoparticles which are synthesized using two kinds of solvents. The obtained lattice constants are summarized in Table 1, in which the data of Pt nanoparticle and bulk Pd are also shown. The lattice constants of Pd nanoparticles, synthesized by polyol process, are larger than that of the bulk Pd and moreover, than that of the Pt nanoparticles synthesized by polyol process, where the lattice constant of Pd is smaller than that of Pt in bulk. This indicates that Pd nanoparticles include some impurities in Pd lattice so as to increase the lattice constants. In addition, the expansion of lattice in Pd nanoparticles using dioctyl ether is larger than that using diphenyl ether. This indicates that the substitution of diphenyl ether for dioctyl ether reduces the impurity in Pd nanoparticles.

In FePd nanoparticles the similar tendency is observed, i.e. the impurity content is larger in FePd nanoparticles synthesized using dioctyl ether.

The XPS data of the Pd nanoparticles, synthesized using dioctyl ether and diphenyl ether, are shown in Table 2. In addition, the XPS data of Pd nanoparticles, prepared by gas evaporation method, are also shown for comparison. The binding energies of the as-made Pd nanoparticles were 335.1–335.2 eV (Pd 3d₅/₂) and 340.3–340.5 eV (Pd 3d₃/₂) independent of solvents. These binding energies are the same as those of the bulk Pd and the Pd nanoparticles prepared by gas evaporation. In addition, the binding energies are intrinsically constant even after annealing at 600 °C. These XPS data suggest that the impurity in Pd nanoparticles, synthesized by polyol process, does not form the rigid binding state with the Pd matrix. This indicates that the impurity in Pd nanoparticles is not substitutional but interstitial.

In order to specify the element of interstitial impurities, EPMA was used. As a result, carbon was exclusively detected other than Pd in the Pd nanoparticle sample. The result of EPMA indicates that only specified C atom can be impurity element mixed in the Pd nanoparticles, although C atoms are

| Table 1 | Lattice constant of FePd nanoparticles synthesized by polyol process by X-ray diffraction patterns |
|----------|--------------------------------------------------|
|          | Nanoparticles | Bulk (Å) |
|          | Diphenyl ether | Dioctyl ether |
| Pd       | 3.937 Å       | 3.961 Å     | 3.890 |
| Pt        | 3.929 Å       | 3.923      |
| FePd     | 3.869 Å (Fe₄₇,Pd₅₂.₉) | 3.895 Å (Fe₄₉,Pd₅₀.₉) |

The date of pure bulk Pd and Pt are also shown.
This suggests that Pd nanoparticles form the Pd$_{1-x}$C$_x$ solid solution. It was reported that the Pd$_{1-x}$C$_x$ phase, having fcc structure, was formed by heating the Pd in an atmosphere of ethylene, acetylene or carbon monoxide [6]. The maximum amount of carbon atoms in Pd$_{1-x}$C$_x$ phase is $x=0.15$, and the solid solution is metastable and decomposes at temperatures above 600 °C at which the expulsion of C atoms occurs [7].

Fig. 5 shows the XRD patterns of Pd and Fe$_{54.5}$Pd$_{45.5}$ nanoparticles synthesized by the modified polyol process using dioctyl ether. The lattice constants, obtained by the XRD peaks, are shown in Table 3. The lattice constant of Pd nanoparticles decreased as the temperature for annealing increases and down to 3.908 Å after the 700 °C annealing. This suggests that Pd nanoparticles form the Pd$_{1-x}$C$_x$ solid solution, because the expulsion of C atoms from the Pd$_{1-x}$C$_x$ is significantly induced by annealing at temperatures above 600 °C. In FePd nanoparticles, similarly, the lattice constant decreased by annealing. Therefore, we estimate that the FePd nanoparticles also include C atoms and the expulsion of C atoms occurs by annealing. Based on the relation between the lattice constant and the C concentration in bulk Pd$_{1-x}$C$_x$ [8], we can evaluate the amount of C atoms in the as-made sample, synthesized in dioctyl ether, to be 8.7% and that in the 700 °C-annealed sample to be 2.2% according to the Vegard’s law. On the other hand, the amount of interstitial C atoms in as-made Pd nanoparticles, synthesized using diphenyl ether, is 5.7%. Thus, the 3% decrease in C concentration is induced by changing the solvent from dioctyl ether to diphenyl ether. In other words, the Pd or FePd nanoparticles with less impurity can be obtained using diphenyl ether as solvent in the synthesis process. We note that the lattice constant of Pt, synthesized in dioctyl ether, scarcely changes from that in bulk Pt as shown in Table 1. Therefore, we estimate that the admixture of interstitial C atom is negligible in chemical preparation process of Pt and FePt nanoparticles.

The impurities in FePd nanoparticles form the interstitial solid solution. Therefore, a large amount of interstitial C atoms significantly interrupt the thermal diffusion of Fe and Pd atoms during the thermal treatment so as to prevent the transformation to L1$_0$ structure. This is the case of the FePd nanoparticles synthesized using dioctyl ether. The decrease in C concentration in FePd nanoparticles, synthesized using diphenyl ether, leads to the high diffusion rate of atoms during the thermal treatment so as to induce the L1$_0$ transformation in FePd nanoparticles.

The mechanism for the introduction of C impurity into Pd or FePd nanoparticles may be complicatedly related to various parameters such as the dissolubility of Pd(acac)$_2$ in solvent and the concentration of Pd(acac)$_2$. In order to explain the relation between the solvents used with the reflux and the amount of the C impurity in the synthesis of Pd or FePd nanoparticles, the further work, based on the characterization techniques to monitor the synthesis process, is needed.

### 4. Conclusions

FePd nanoparticles were synthesized by the modified polyol process that is improved from the procedure previously reported. We succeeded to realize the transformation to L1$_0$ structure after annealing at 600 °C in FePd nanoparticles synthesized using thermal decomposition of Fe(CO)$_3$. In addition, we confirmed that the coercivity in the FePd nanoparticles, synthesized by the modified polyol process, increases by the transformation to L1$_0$ structure. We found that FePd nanoparticles included interstitial C atoms in the synthesis process, and the transformation to L1$_0$ structure after annealing is prevented through the interruption of thermal diffusion of Fe and Pd atoms, which is caused by the interstitial C atoms. The mixture of impurities in the chemical synthesis of
FePd nanoparticles is essential for the transformation to L1₀ structure.

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