High-Coercivity Fe-Co Nanoparticles Prepared by Pulsed Arc Plasma Deposition

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Fe-Co nanoparticles were prepared on SiO2 nanoparticles by a pulsed arc plasma deposition (APD) method and the influence of discharge count during APD on the microstructure and magnetic properties of the nanoparticles was investigated. When the discharge count was 300 shots, the average particle size (d50) of Fe-Co was 3.7 nm and an unusually high coercivity (Hc) of 300 kA·m⁻¹ was obtained. The average particle size increased and the coercivity decreased with increasing discharge count. Fe-Co nanoparticles deposited on C nanoparticles using a discharge count of 300 shots exhibited a lower coercivity than that of Fe-Co nanoparticles deposited on SiO2 nanoparticles.

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1. Introduction

Many researchers have investigated approaches for fabricating magnetic nanoparticles because they are promising for various technical applications such as nanocomposite magnets, recording media, and drug delivery systems.1-3) As Fe-Co has a high saturation magnetic polarization, several methods have been developed to synthesize Fe-Co nanoparticles. Chemical methods,4-8) such as the polyol method4) and hydrogen reduction method,5) allow the size and composition of the nanoparticles to be controlled, but it is difficult to prevent aggregation of the particles during the drying process. Fe-Co nanoparticles can also be prepared by physical vapor deposition methods, such as the metal vapor method.9,10) Physical vapor deposition methods provide metal nanoparticles with higher purity and crystallinity than chemical methods.11) Therefore, we focused on the pulsed arc deposition (APD) method. Discharge of the arc to the target vaporizes and ionizes the target, and fine particles are deposited on the substrate or particles. The APD method allows control of nanoparticle morphology by controlling deposition conditions such as deposition pressure, atmosphere, discharge voltage, and discharge count.12) To our knowledge, this is an first report of the investigation on the microstructure and magnetic properties of Fe-Co nanoparticles on several nanoparticles prepared by APD at this time.

2. Experimental Procedure

The Fe-Co nanoparticles were prepared by using a pulsed arc plasma deposition system with a base pressure of about 2 × 10⁻³ Pa. The experimental setup is shown schematically in Fig. 1. The composition of the target was Fe₇₀Co₃₀ (at%), and it was deposited on SiO₂ or C nanoparticles with an average particle size of 70 or 100 nm, respectively. The discharge voltage was 200 V, and the discharge count was varied from 100 to 1000 shots. Deposition was conducted under a flow of Ar and He gas.

The microstructure of the produced nanoparticles was observed by transmission electron microscopy (TEM). Particle size distributions were evaluated from TEM images, and the cumulative 10%, 50%, and 90% fractions are defined as d₁₀, d₅₀, and d₉₀, respectively. The average particle size was defined as the median diameter (d₅₀), and the particle size distribution was defined as the relative span (RS) according to the following equation:

\[
RS = \frac{d₉₀ - d₁₀}{d₅₀}
\]  

The M-H loops were measured by using a vibrating sample magnetometer (VSM) at fields up to 1400 kA·m⁻¹ at room temperature. Before the VSM measurements, the particles were aligned with an applied magnetic field of 1600 kA·m⁻¹ and fixed with paraffin wax, then magnetized in a pulsed magnetic field of 6400 kA·m⁻¹. Obtained raw M-H loops were downward-sloping due to the diamagnetic terms originating from the sample holder, sample capsule, paraffin wax, and SiO₂ or C nanoparticles. The diamagnetic term originating from the sample holder was corrected for by subtracting the M-H loop of the sample holder from raw M-H loop. Then the residual diamagnetic terms were corrected by setting the slope of the M-H loop (dM/dH) to zero at the maximum field. Since it was difficult to evaluate the weight of Fe-Co nanoparticles on SiO₂, the magnetization was...
calculated for the combined weight of the SiO2 and Fe-Co nanoparticles.

3. Results and Discussions

Figure 2 shows the TEM images of the Fe-Co nanoparticles deposited on SiO2 nanoparticles, which were prepared using a discharge count of (a) 300 and (b) 1000 shots. A TEM image of a SiO2 nanoparticle without deposition of Fe-Co nanoparticle is shown in Fig. 2(c). The bare SiO2 nanoparticles are spherical and have homogeneous contrast at their surface (Fig. 2(c)). However, when Fe-Co nanoparticles are present, areas of dark contrast are evident on the surface of the SiO2 nanoparticles (Fig. 2(a) and (b)). A magnified TEM image of the boxed area in Fig. 2(a) is presented as an inset and shows that the Fe-Co particles prepared using a discharge count of 300 shots are several nanometers in size. The Fe-Co particles prepared using a discharge count of 1000 shots are shown in Fig. 2(b) and they are about 10 nm in size. Therefore, the Fe-Co particle size tended to increase as the discharge count was increased.

The particle size distribution of the Fe-Co nanoparticles was evaluated from the TEM images. Figure 3 shows the particle size distribution and cumulative fraction of the Fe-Co nanoparticles, as well as the average particle size ($d_{50}$) and relative span ($RS$). Fe-Co nanoparticles prepared using a discharge count of 300 shots had $d_{50}$ of 3.7 nm and $RS$ of 0.62, whereas $d_{50}$ and $RS$ of the Fe-Co nanoparticles prepared using a discharge count of 1000 shots increased to 6.7 nm and

![Fig. 2 TEM images of Fe-Co nanoparticles deposited on SiO2 nanoparticles using a discharge count of (a) 300 or (b) 1000 shots, and (c) a TEM image of SiO2 nanoparticles without deposition of Fe-Co.](image)

![Fig. 3 Particle size distributions of Fe-Co nanoparticles deposited on SiO2 nanoparticles using a discharge count of (a) 300 or (b) 1000 shots.](image)

![Fig. 4 Dependence of (a) saturation magnetization ($\sigma_s$) and (b) coercivity ($H_c$) on discharge count of Fe-Co nanoparticles deposited on SiO2 nanoparticles.](image)
1.1, respectively. These results indicate that aggregation and grain growth of Fe-Co nanoparticles occur with increasing discharge count. Since microstructural changes can influence the magnetic properties of the nanoparticles, the dependence of saturation magnetization and coercivity on the discharge count was measured.

Figure 4 shows the changes in the saturation magnetization ($\sigma_s$) and coercivity ($H_c$) of Fe-Co nanoparticles as a function of discharge count. $\sigma_s$ increases monotonically with increasing discharge count, indicating that the volume fraction of Fe-Co also increased with increasing discharge count. In contrast, Fig. 4(b) shows high coercivity for Fe-Co nanoparticles prepared using a discharge count of 100–300 shots, then the coercivity decreased with increasing discharge count. The maximum coercivity value was 300 kA·m$^{-1}$ for the Fe-Co nanoparticles prepared using a discharge count of 300 shots and their $d_{50}$ was 3.7 nm, as mentioned above. This coercivity is considerably higher than the previously reported values for Fe-Co nanoparticles.$^{4-11}$ The coercivity of magnetic materials is known to increase with decreasing particle size,$^{13}$ but the coercivity obtained in this study was quite high. The coercivity of the Fe-Co nanoparticles decreased with increasing discharge count, likely due to aggregation and grain growth of the Fe-Co particles.

Many researchers have reported origins of the high coercivity in Fe-Co-based systems,$^{14-20}$ which are listed in Table 1: (i) magnetocrystalline anisotropy, (ii) shape anisotropy, (iii) exchange anisotropy, (iv) magnetoelastically induced anisotropy, and (v) surface and interfacial anisotropy.

High magnetocrystalline anisotropy is responsible for the coercivity of many magnetic materials. For example, CoFe$_2$O$_4$ (Co-ferrite) with a spinel-type structure (space group: No. 227) has a high magnetocrystalline anisotropy ($K_1$) of $4 \times 10^5$ J·m$^{-3}$,$^{14,16}$ and CoFe$_2$O$_4$ nanoparticles show a high coercivity of 750 kA·m$^{-1}$, as we reported previously.$^{15}$ Higher magnetocrystalline anisotropy can also be caused by lattice distortion of the Fe-Co crystal. First-principles calculations have shown that Fe-Co alloy can have a high uniaxial magnetocrystalline anisotropy ($K_u$) of up to $10^3$ J·m$^{-3}$ when its lattice is distorted into a bct crystal.$^{21,22}$ The crystal structure of Fe-Co nanoparticles deposited on SiO$_2$ nanoparticles was therefore investigated by TEM. A high-resolution TEM image is shown in Fig. 5(a), the fast Fourier transformation (FFT) pattern of the Fe-Co nanoparticle indicated with a white arrow in Fig. 5(a) is shown in Fig. 5(b), and a simulation pattern for (b) is shown in Fig. 5(c). The TEM image in Fig. 5(a) shows that lattice fringes were observed in some Fe-Co nanoparticles. The FFT pattern of Fig. 5(b) corresponds to a bcc or B2 structure with the zone axis in a (111) direction. It is well known that Fe-Co alloy has a B2 structure (space group: No. 221) in the equilibrium state.$^{23}$ However, obvious superlattice spots originating from the B2 structure have not been confirmed. This means that the Fe-Co nanoparticles are bcc or B2 with low ordering. Although it is unclear whether the Fe-Co nanoparticles are in the bcc or B2 structure, the FFT pattern shows that the matrix phase of the Fe-Co nanoparticles does not have the fcc or bct structure. Since both bcc and B2 Fe-Co have a low magnetocrystalline anisotropy constant of about $10^4$ J·m$^{-3}$, the appearance of a matrix phase with a high magnetocrystalline anisotropy in Fe-Co nanoparticles is unlikely to be the cause of the high coercivity observed here.

### Table 1: Contributions of magnetic anisotropy to enhanced coercivity in Fe-Co-based systems.

<table>
<thead>
<tr>
<th>Magnetic anisotropy</th>
<th>System</th>
<th>Anisotropy constant, $K$</th>
<th>Coercivity, $H_c$/kA·m$^{-1}$</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magneto-crystalline</td>
<td>CoFe$_2$O$_4$ nanoparticle</td>
<td>$4 \times 10^5$ J·m$^{-3}$</td>
<td>750</td>
<td>14, 15</td>
</tr>
<tr>
<td>Shape</td>
<td>Fe-Co-Co alloy</td>
<td>—</td>
<td>51.7</td>
<td>16</td>
</tr>
<tr>
<td>Exchange</td>
<td>Fe/FeO</td>
<td>$\sim 10^3$ J·m$^{-3}$</td>
<td>271</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Co/CoO</td>
<td>$\sim 10^3$ J·m$^{-3}$</td>
<td>137</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>core/shell particle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetoelectrically induced</td>
<td>Fe granular film</td>
<td>$&lt;80$ J·m$^{-3}$</td>
<td>—</td>
<td>19</td>
</tr>
<tr>
<td>Surface, Interfacial</td>
<td>Fe/SiO$_2$ granular film</td>
<td>$4.2 \times 10^{-4}$ J·m$^{-3}$</td>
<td>48</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Co$_3$FeAl/MgO thin film</td>
<td>$10^{-3}$ J·m$^{-2}$</td>
<td>44</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 5. (a) High-resolution TEM image of Fe-Co nanoparticles on SiO$_2$ nanoparticles prepared using a discharge count of 300 shots, (b) FFT pattern of the Fe-Co nanoparticle indicated with a white arrow in (a), and (c) simulation pattern for (b).
Elongated magnetic particles induce shape anisotropy because the magnetization vector preferentially lies along the elongated axis in order to minimize the demagnetizing factor. For example, the relatively high coercivity of Fe-Cr-Co magnets derives from shape anisotropy of elongated ferromagnetic Fe-Co in the nonmagnetic Cr-rich matrix phase, and a coercivity of up to 51.7 kA·m⁻¹ has been reported for Fe-Cr-Co magnet.¹⁰ Thus, it is possible that shape anisotropy enhanced the coercivity of the Fe-Co nanoparticles prepared in this study. However, as the TEM image in Fig. 5(a) shows, Fe-Co nanoparticles prepared by APD are spherical, indicating that shape anisotropy likely plays a negligible role in inducing the observed high coercivity of Fe-Co nanoparticles.

Exchange anisotropy has been reported for core-shell Fe/FeO¹⁷ and Co/CoO¹⁸ particles showing relatively high coercivity. The metal core is ferromagnetic and the oxide shell is antiferromagnetic below its Néel temperature. Exchange-coupling of the core and oxide shell results in an exchange-bias effect and the M-H loop shifts to the second quadrant, leading to improved coercivity. The magnetic properties of the Fe-Co nanoparticles were measured at room temperature in the current study; consequently, the exchange anisotropy between the Fe-Co core and FeO or CoO shell should be negligible since the Néel temperatures of FeO and CoO are 185 K and 270 K, respectively.¹⁸,²⁴

It has been proposed that magnetoelastically induced anisotropy possibly enhances the coercivity of some Fe/SiO₂ granular films.¹⁹ However, it was previously reported¹⁹ that this magnetoelastic energy is about 80 J·m⁻², which is much smaller than the magnetocrystalline anisotropy energy. Therefore, magnetoelastically induced anisotropy contributes negligibly to the induction of high coercivity in the current study.

Consequently, magnetocrystalline anisotropy, shape anisotropy, exchange anisotropy, and magnetoelastically induced anisotropy do not satisfactorily explain the anomalously high coercivity of 300 kA·m⁻¹ for the Fe-Co nanoparticles prepared on the SiO₂ nanoparticles. Surface anisotropy and interfacial anisotropy are discussed below as possible origins of this high coercivity.

In a previous study, Chen et al.¹⁹ reported an Fe/SiO₂ granular film with a relatively high coercivity of 48 kA·m⁻¹ and investigated the particle size dependence of coercivity. The uniaxial surface anisotropy constant (Kₐ) of Fe nanoparticles was evaluated from the Hₑ₋d curve and reported to be 4.2 × 10⁻⁴ J·m⁻². The authors of the study concluded that the uniaxial surface anisotropy is responsible for enhanced coercivity of the Fe/SiO₂ granular films.¹⁹ Gangopadhyay et al. reported that fine Fe particles with diameters of 5–20 nm have a higher coercivity of 83.6 kA·m⁻¹¹⁷ than bulk α-Fe, and that non-continuous Fe oxides of several nanometers in diameter were present on the surface of α-Fe particles. They also stated that there was interaction between Fe oxide and α-Fe, and suggested that this interfacial interaction could induce the higher coercivity. In this study, the TEM observations and FFT analysis of the Fe-Co nanoparticles (Fig. 5) indicated that the Fe-Co structure was bcc or B2. This means that the Fe-oxide phase was not observed by TEM. However, the TEM observation and FFT analysis were carried out at the surface of the Fe-Co nanoparticles and therefore we cannot rule out the possibility that Fe oxide phase was present at the Fe-Co/SiO₂ interface and caused the high coercivity.

The induction of interfacial anisotropy between Fe and MgO in thin films has been reported,²⁵ and it has been suggested that hybridization of the Fe-3d and O-2p orbitals can improve interfacial anisotropy: a value of about 10⁻¹² J·m⁻² has been estimated.²⁰,²⁵

Thus, the collective evidence to date suggests that surface anisotropy, interfacial anisotropy, or both, could enhance the coercivity of the Fe-Co nanoparticles prepared in this study. We considered that O atoms in the SiO₂ nanoparticles could enhance the interfacial anisotropy as described above. To investigate the influence of O in the SiO₂ nanoparticles on the coercivity of the Fe-Co nanoparticles, we were deposited on C nanoparticles instead of SiO₂ to use a material free of O. Figure 6 shows the hysteresis loop of Fe-Co nanoparticles deposited on C nanoparticles in comparison with that on SiO₂ nanoparticles, in which the vertical axis is normalized to σ/σ₀. As described above, Fe-Co nanoparticles deposited on SiO₂ nanoparticles have a high coercivity value of about 300 kA·m⁻¹; in contrast, Fe-Co nanoparticles deposited on C had rather low coercivity (Fig. 6). This result indicates that SiO₂ can play an important role in improving the coercivity of Fe-Co nanoparticles.

Consequently, this study suggests that the surface anisotropy and/or interfacial anisotropy of Fe-Co/SiO₂ are the most likely causes that induce high coercivity of Fe-Co nanoparticles. Further work is required to elucidate the origin of the high coercivity.

4. Conclusion

Fe-Co nanoparticles were prepared using the pulsed arc plasma deposition method. Fe-Co nanoparticles deposited on SiO₂ nanoparticles using a discharge count number of 300 shots showed an average particle size (d₅₀) of 3.7 nm and a high coercivity (Hₑ) of 300 kA·m⁻¹. FFT analysis revealed that the crystal structure was bcc or B2. The average particle size increased and coercivity decreased with increasing discharge count. We also deposited Fe-Co nanoparticles on C nanoparticles using a discharge count of 300 shots; the coercivity of these particles was markedly lower than that of
the Fe-Co nanoparticles on SiO₂. Our results suggest that the interface between Fe-Co and SiO₂ influences their magnetic anisotropy, and can enhance the coercivity of Fe-Co nanoparticles.

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REFERENCES