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Magnetic Properties of Encapsulated Co Nanoparticles Prepared with Reversed Micelle

Tetsuji Haeiwa, Motohiro Wada and Shozi Mishima
Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553 Japan
Fax: 81-26-269-5495, e-mail: haeiwa@cs.shinshu-u.ac.jp

Magnetic properties and thermal stabilities of cobalt nanoparticles encapsulated in SiO_2 prepared with the reversed micelle technique in the absence of water were investigated. The encapsulated Co nanoparticles have been synthesized with a reversed micelle. The nanoparticles have uniformly distributed with an average diameter of 2.4 nm. The magnetization curves of the encapsulated Co nanoparticles exhibit the superparamagnetic nature. From the analysis based on the Langevin function with the log-normal distribution, a mean diameter of magnetic particles was 2.9 nm, consistent with the TEM. The Co nanoparticle is thermally stable up to 373K. The growth of the particles inside the capsule without crystallization was observed after annealing at 523 K. The crystallization and the grain growth of Co nanoparticles were observed after annealing above 760 K.

Key words: Co nanoparticle, SiO_2 capsule, superparamagnetism, reversed micelle, thermal stability

1. INTRODUCTION

Nanoparticles have been the subject of intense research in recent years. The preparation of nanoparticles in a reverse micelle system has attracted great attention because of its possibility to obtain mono-dispersed particles in nm size[1]. Water pool in the reverse micelle cage is characterized by the water-surfactant molar ratio (w = $[H_2O]/[S]$). The size of the reverse micelle cages can be varied by w. Therefore, the size of the particles formed inside micelle also usually depend on w[2].

Generally the nanoparticles tend to aggregate each other and to make large aggregations. It is possible to prevent the aggregation of the particles by modifying the surface. Tailoring the surface properties of nanoparticles often accomplished by coating the particles or encapsulating them within a shell[3]. The surface coating of inorganic-SiO_2 can be considered to be a good protection against aggregate[4]. The SiO_2 coating is generally carried out by hydrolysis of the TEOS (tetraethoxysilane) in alcoholic solution with water[5]. (This method is known the Stöber process[6].) A particle coalescence and a increase of the particle size as a result by high temperature anneal for the crystallization is a problem[7]. It is expected that grain growth of the nanoparticles by annealing will be suppressed to the higher temperature by the exsistence of the inorganic silica of the nanoparticle surface. In a reversed micelle system, however, the condition of the reverse micelle cage is made to change by the addition of alcohol and water. We are investigating the hydrolysis of TEOS inside reverse micelle cage without the additional alcohol. Previous work showed that both reaction to reduce $CoCl_2$-$6H_2O$ and hydrolysis of TEOS could be carried out inside a reversed micelle cage which synthesize the encapsulated Co nanoparticles[4]. However, the number of the particle in a micelle was more dependent on w rather than the size of the particle[4]. Therefore, it is necessary to reduce the amount of water molecules in order to get an encapsulated nanoparticle.

In this study, the preparation of cobalt nanoparticles encapsulated in SiO_2 with the reversed micelle technique without additional water except for crystal water, and their magnetic properties and thermal stabilities were investigated.

2. EXPERIMENTAL

Co nanoparticles were synthesized in the binary system of DDAB/toluene, where DDAB (didodecyldimethyl-ammonium bromide) is a cationic surfactant. Sodium borohydride, $NaBH_4$, was used to reduce $CoCl_2$-$6H_2O$ to obtain Co nanoparticles. To encapsulate Co nanoparticles, TEOS was added into the dispersed solution of Co nanoparticles, and the hydrolysis of TEOS was carried out at 333 K for 72 hours. In the previous work, the aggrigation of capsules during drying was observed[3], since the active -OHs on silica capsule surface exists after the hydrolysis. To eliminate the additional aggregations between the surface -OHs of silica capsules, the surface -OH of silica capsules was modified with HMDS (hexamethyldisilazane) into non-reactive -CH_3.

The samples were characterized by using TEM (JEOL, JEM-2010), XRD (Rigaku, RINT-2200V), and VSM (TOEI KOGYO, VSM-5S).

3. RESULTS AND DISSCUSSION

Figure 1 shows the TEM image and selected area

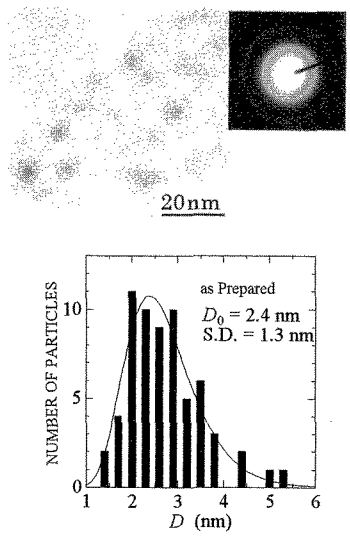

Fig.1 TEM image and selected area electron diffraction pattern of the SiO_2 encapsulated Co nanoparticles and corresponding size histogram.

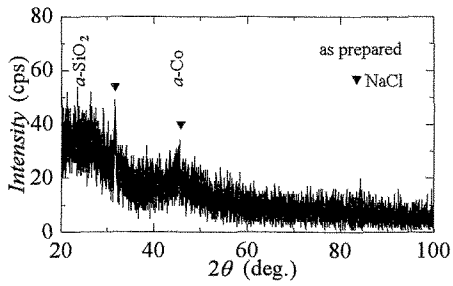

Fig. 2 X-ray diffraction pattern of the SiO_2 encapsulated Co nanoparticles.

electron diffraction pattern of the SiO_2 encapsulated Co nanoparticles and corresponding size histogram. The well dispersed single Co nanoparticles with silica shell were observed. The size distribution can be calculated using the following log-normal distribution function [8],

$$f(D) = \frac{1}{\sqrt{2\pi}\ln s}\exp\left(-\frac{(\ln D - \ln D_0)^2}{2\ln^2 s}\right) \quad (1)$$

where s is the diameter standard deviation and D_0 is the mean diameter. The average diameter of the Co nanoparticles was about 2.4 nm with a standard deviation = 1.3 nm. The average thickness of the silica capsule was about 2.2 nm. Only the halo rings are observed in the selected area electron beam diffraction.

Figure 2 shows the X-ray diffraction pattern of encapsulated Co nanoparticles. The broad diffraction peaks from the amorphous silica and the amorphous Co are observed near 2θ = 25 deg. and 2θ = 45 deg., respectively. In our sample, the clear evidence that the Co particle is crystalline has not been obtained.

Figure 3 shows magnetization as a function of applied field measured at room temperature and

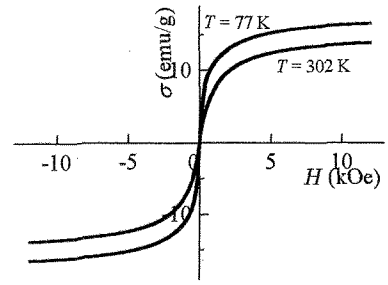

Fig. 3 Magnetization curves as a function of applied magnetic field for the SiO_2 encapsulated Co nanoparticles measured at 303 K and 77 K.

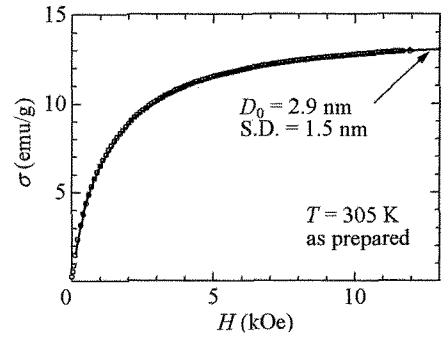

Fig. 4 Experimental and calculated magnetization curve as a function of applied field of the SiO_2 encapsulated Co nanoparticles. The circles indicate the experimental data. The solid line is the calculated values of eq.(1) and eq.(2).

at 77 K. Both magnetization curves exhibit no hysteresis and unsaturation characteristics, indicating that the Co nanoparticles are superparamagnetic nature. For superparamagnetic particles, the true magnetic moment at a particular temperature can be calculated using the Langevin function [9],

$$M = N\mu L\left(\frac{\mu H}{k_B T}\right) \quad (2)$$

where μ ($=M_s\pi D^3/6$) is the true magnetic moment of each particle (M_s is the saturation magnetization of a particle, D is the diameter of a particle), k_B is the Boltzmann constant, T is the absolute temperature, N is the number density and $L(x)$ (= *coth* x - $1/x$) is the Langevin function. The magnetization is shown in the summation of the Langevin functions of each particle, when there is a distribution in the grain size. Figure 4 shows the analysis in the experimental magnetization curve measured at 303 K using the Langevin functions with the log-normal size distribution. Here, the open circles indicate the experimental data and the solid curve is the calculations from eq. (1) and eq. (2) with M_s = 1422 emu/cm^3. This result indicates that a mean diameter D_0 determined in this way is 2.9 nm with a standard deviation = 1.5 nm, which is close to the particle size observed from TEM (2.4 nm).

It is expected that grain growth of the nanoparticles

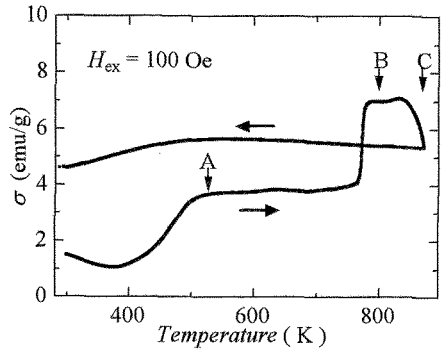

Fig. 5 Temperature dependence of the magnetization at H = 100 Oe.

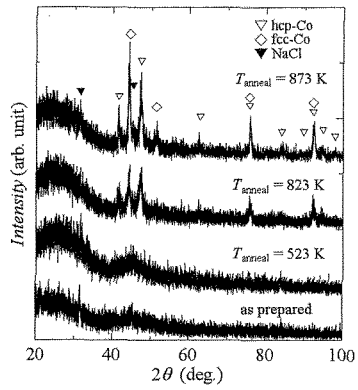

Fig. 6 X-ray diffraction patterns of the SiO_2 encapsulated Co nanoparticles after annealing at T_{anneal} = 523 K, 823 K and 873 K.

by annealing will be suppressed to the higher temperature by the inorganic silica on the nanoparticle surface. We examined the thermal stability of the SiO_2 encapsulated Co nanoparticles by measuring temperature dependence of the magnetization. The magnetization was measured up to 873 K in heating rate of 2 degrees per minute by applying magnetic field 100 Oe in the vacuum (<10^{-3} Pa).

Figure 5 shows the temperature dependence of magnetization. The magnetization gradually increases between 350 K and 500 K and is almost constant from 500 K to near 760 K. As farther increasing temperature, it rapidly increases at about 760 K and rapidly decreases above 870 K. The result of temperature dependence of the magnetization suggests the structural changes of the Co nanoparticles at 270K, 760K and 870K. The samples annealed up to 523K, 823K and 873K, which annealing temperatures were indicated as A, B and C in Fig. 5 respectively, were prepared, and their X-ray diffractions and magnetization curves were measured.

Figure 6 shows the annealing temperature dependence of X-ray diffraction patterns. The diffraction peaks which indicated the crystallization of Co were observed after annealing at 823K.

Figure 7 shows the TEM image of the SiO_2 encapsulated Co nanoparticles after annealing at 523 K and corresponding size histogram. The Co nanoparticles with silica shell were still observed. Neither breaking of the silica wall nor increase in the diameter of the silica shell was observed. The

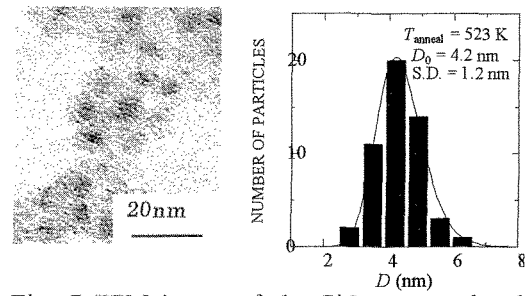

Fig. 7 TEM image of the SiO_2 encapsulated Co nanoparticles after annealing at T_{anneal} = 523 K and corresponding size histogram.

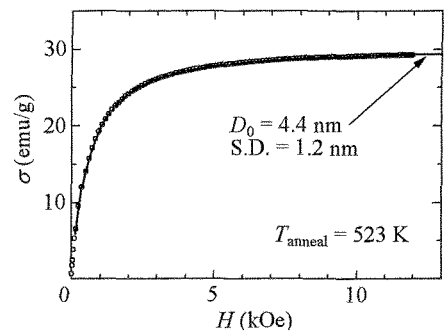

Fig. 8 Experimental and calculated magnetization curve as a function of applied field of the SiO_2 encapsulated Co nanoparticles after annealing at T_{anneal} = 523 K. The circles indicate the experimental data. The solid line is the calculated values of eq.(1) and eq.(2).

average diameter of the Co nanoparticles calculated of eq. (1) was 4.2 nm with a standard deviation = 1.2 nm which increased at the size of the double before anneal. The average diameter of the SiO_2 was about 7 nm and does not change after annealing at 523 K.

The magnetization curve of Co nanoparticles after annealing at 523 K measured at room temperature exhibits no hysteresis and unsaturation characteristics, indicating that the Co nanoparticles are still superparamagnetic nature after anneal. Figure 8 shows the analysis in the experimental magnetization curve of the Co nanoparticles after annealing at 523 K measured at 303 K using the Langevin functions with the log-normal size distribution. Here, the open circles indicate the experimental data and the solid curve is the calculations from eq. (1) and eq. (2) with M_s = 1422 emu/cm^3. This analysis indicates that a mean diameter D_0 determined in this way is 4.4 nm with a standard deviation = 1.2 nm, which is close to the particle size observed from TEM (4.2 nm).

Figure 9 shows magnetization curves of Co nanoparticles after annealing at 823 K and 873 K measured at room temperature. Both magnetization curves exhibit hysteresis. The Co nanoparticles after annealing above 823 K are ferromagnetic nature and these coercive forces

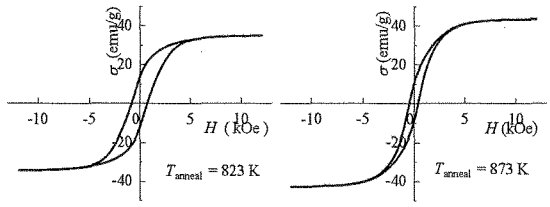

Fig. 9 Magnetization curves as a function of applied magnetic field for the SiO_2 encapsulated Co nanoparticles annealed at 823 K and 873 K measured at 303 K.

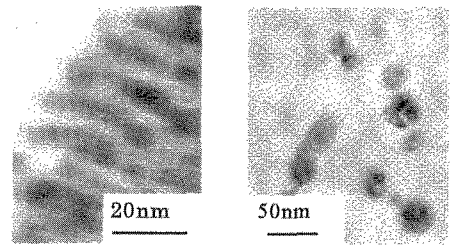

Fig. 10 TEM images encapsulated Co nanoparticles after annealing at 873 K.

and saturation magnetizations are 770 Oe, 36 emu/g and 430 Oe, 44 emu/g for the Co nanoparticles after annealing at 823 K and 873 K respectively.

Figure 10 shows the TEM image of the SiO_2 encapsulated Co nanoparticles after annealing at 873 K. Large particles of the about 50 nm diameter is also observed, while the particles of the about 5 nm diameter that separated in the silica still exists. The appearance of the ferromagnetism after annealing above 823 K seems to originate from increase of the grain size and crystallization of the particles which combined together though breaking of the silica wall.

These results suggest that (1) silica is hollow capsule with about 7 nm diameter rather than surface coat with the 2.2 nm thickness, (2) the reduction of the Co ion is not sufficient under the poor water environment, and nonmagnetic Co or Co-compounds remain in the SiO_2 capsule, (3) by anneal up to 760 K, nonmagnetic Co or Co-compounds in the capsule decompose and combine with a Co particle which causes an increase of the particle size, (4) by annealing above 760 K, the part of the silica wall is broken, and a particle coalescence occurs which causes an increase of the particle size and an appearance of the ferromagnetism.

4. CONCLUSION

The encapsulated Co nanoparticles have been synthesized with a reversed micelle. The nanoparticles have a uniformly distributed with an average diameter of 2.4 nm. The magnetization curves of the encapsulated Co nanoparticles exhibit the superparamagnetic nature. From the analysis based on the Langevin function with the log-normal distribution, a mean diameter of magnetic particles was 2.9 nm, consistent with the TEM. Co nanoparticle is thermally stable up to 373 K. The growth of the particles inside the capsule without crystallization was observed after annealing at 523 K. The crystallization and the grain growth of Co nanoparticles were observed after annealing above 760 K. Details of the chemical and physical structures of the SiO_2 capsule inside are the subject of further studies.

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