Magnetic properties of nanophase cobalt particles synthesized in inversed micelles

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Cobalt particles were prepared with the microemulsion method in the binary system of DDAB (didodecyldimethylammonium bromide)/toluene by reduction of $CoCl_2$ with $NaBH_4$. The average particle size of the as-prepared samples could be varied from 1.8 to 4.4 nm by controlling the concentration of $CoCl_2$ in the solution of DDAB in toluene. TEM studies showed that the particles were quite uniform and well isolated. The particle sizes determined from magnetic data were consistent with those measured by TEM. The coercivity of the particles at 10 K increased from 640 to 1250 Oe as particle size increased from 1.8 to 4.4 nm. The blocking temperature of the particles increased from 19 to 50 K for the same size range. The saturation magnetization σ_s at 2 K increased with decreasing particle size. The value of σ_s of the particles with average size of 1.8 nm was about 200 emu/g, which is 20% higher than the bulk value. This implies that the magnetic moment per atom is enhanced in the nanoparticle system.

I. INTRODUCTION

Nanoscale materials show novel properties that are often significantly different from the bulk due to fundamental changes in coordination, symmetry, and confinement. In magnetic materials advantage has been taken, for a considerable time, of the variation of magnetic properties of fine particles due to effects such as single domains, superparamagnetism, and surface interaction. Only recently, however, have magnetic studies proceeded into the ultrasmall regions where more fundamental changes will occur as the bulk transforms to the atomic. In this work we describe the synthesis of nanoscale metallic cobalt particles using an inversed micelle synthesis method. A consistent set of size dependent magnetic data are obtained, the most surprising of which show an enhanced, relative to the bulk, magnetic moment per Co atom.

II. EXPERIMENTAL METHODS

Cobalt particles were prepared by the microemulsion method in the binary system of DDAB/toluene.[1,2] $NaBH_4$ was used to reduce $CoCl_2$ to produce Co particles. First $CoCl_2 \cdot 6H_2O$ was dissolved in a deoxygenated 11 wt % DDAB solution in toluene at concentrations of 0.005–0.02 M. The reagent was trapped in the empty micelles and formed a blue transparent solution. Then a 10 M $NaBH_4$ aqueous solution was added on the condition of $[BH_4]:[Co^{2+}]=3:1$ and stirred. It eventually turned from blue to black and formed a stable colloid. The colloid was dried in a glove bag with all the toluene evaporated and formed a paste sample. The cobalt particles were uniformly distributed in the DDAB matrix.

The x-ray spectrum of a paste sample showed only the (111) peak of fcc cobalt. Since the concentration of cobalt in the sample is about 0.6 wt %, the other weaker peaks were in the noise.

When we studied the dependence of the spontaneous magnetization on temperature at low field for zero-field cooled samples, we found that the particles were not pure metallic cobalt when the mole ratio of water to DDAB was much larger than one. Figure 1 shows the data for two samples with the same preparation except the water content. In sample A 60 μl of 5 M $NaBH_4$, whereas in sample B 30 μl of 10 M $NaBH_4$, was added to 10 ml of 0.01 M $CoCl_2$ solution in DDAB/toluene. Sample A shows two peaks in Fig. 1, while its saturation magnetization was just 50% of that of sample B, which had only one peak in σ vs T plot. The two peaks imply two magnetic phases in sample A. In nonmicroemulsion systems we have shown[3] how water causes the borohydrate reduction to create Co_2B whereas Co is created in the absence of water. Thus we interpret the results for sample A to imply that both Co and Co_2B particles
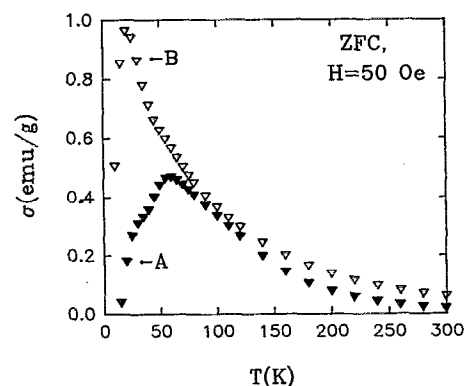

FIG. 1. Temperature dependence of the spontaneous magnetization at $H=50$ Oe for zero-field cooled samples A and B. In sample A 60 μl of 5 M $NaBH_4$, whereas in sample B 30 μl of 10 M $NaBH_4$, was added to 0.01 M $CoCl_2$ solution in DDAB/toluene. The peak at 20 K in both A and B is due to Co; the peak at 60 K in A is due to Co_2B.
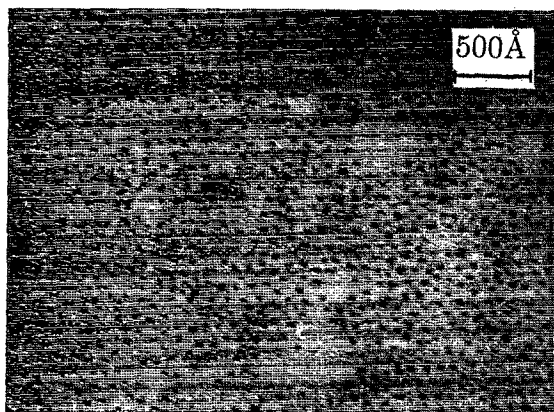
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FIG. 2. TEM photograph of the cobalt particles with an average particle size of 3.3 nm.

FIG. 4. Relation between the anisotropy constant and size of Co particles.

were produced. On the other hand, in sample B only Co is produced. There was, of course, water present in sample B. But at low concentration (one H_2O molecule per DDAB molecule in sample B) the water must be fixed by the hydrophilic part of the DDAB and unable to participate in the Co reduction. We remark that Pileni et al.[4] found the oxidation states of copper metallic clusters changed with the change of water content in the micelles.

With the above results in mind, we controlled the ratio of [H_2O]:[DDAB] below 1.5 to make pure metallic cobalt. The particle size was varied by changing the $CoCl_2$ concentration in the DDAB/toluene system from 0.005 to 0.02 M. We have also tried to increase the particle size by increasing the reaction temperature to 50 °C, but no obvious change was observed.

III. RESULTS AND DISCUSSION

A TEM study was carried out to size the particles and study their morphology. The particle diameter changed from 1.8 to 4.4 nm as the $CoCl_2$ concentration increased from 0.005 to 0.02 M. Figure 2 is a TEM picture of one sample with an average diameter of 3.3 nm. The particles are well separated and their sizes are narrowly distributed.
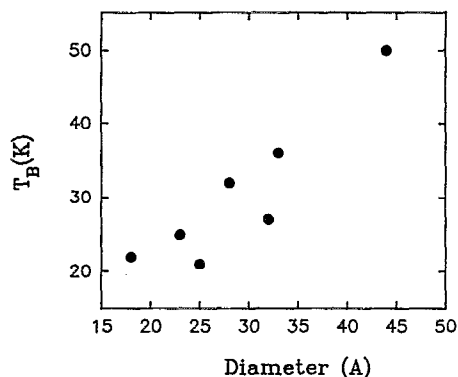
The magnetic properties were measured by a SQUID magnetometer. All the particles were in the superparamagnetic state at room temperature. The sample was cooled in zero field to 2 K, and then magnetization was measured as a function of temperature in a 50 Oe field to determine the blocking temperature. The relation between the blocking temperature and the particle size is shown in Fig. 3. The blocking temperature increased as particle size increased, which is consistent with the behavior of fine particles.

The blocking temperature should roughly satisfy the relationship

$$T_B = \frac{KV}{30k_B},\qquad(1)$$

where K is the anisotropy constant, k_B Boltzmann's constant, and V the average volume of the particle. With the knowledge of the blocking temperature and the particle size, we calculated the anisotropy constant for the Co particles as shown in Fig. 4. The calculated anisotropy is larger than the bulk value of fcc cobalt (2.7×10^6 erg/cm³)[5,6] and increases with the decrease of particle size.

At 10 K, all the samples were in the ferromagnetic state. The coercivities of different samples are shown in Fig. 5. As particle size increased, the coercivity increased, which is the behavior of single-domain particles caused by thermal effects.
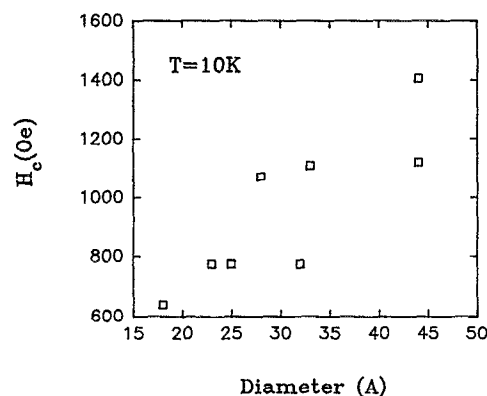

FIG. 3. The blocking temperature as a function of size for Co particles.

FIG. 5. Size dependence of coercivity of Co particles at 10 K.

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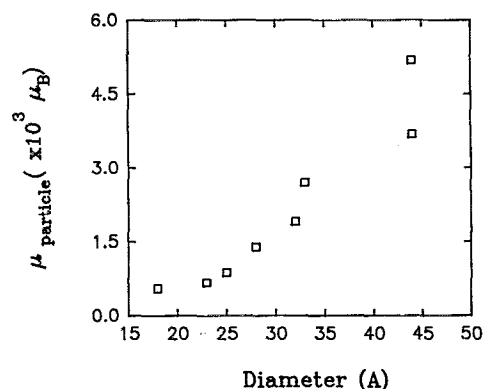
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FIG. 6. Magnetic moment per particle determined from σ_s and susceptibility and for different samples at temperatures higher than T_B.

Above the blocking temperature, the magnetic anisotropy energy barrier of the single-domain particles is overcome by thermal energy and superparamagnetism occurs. The magnetic moment per particle was calculated from the susceptibility and saturation magnetization. The results are shown in Fig. 6 as a function of the TEM determined size.

All the above results are consistent with the properties of ultrafine particles. The saturation magnetization (σ_s) of the cobalt particles at 2 K (Fig. 7) showed surprising behavior. The particles were not saturated even at 5.5 T despite their large moments. To obtain σ_s we plotted σ vs $1/H$ and extrapolated to $1/H \to 0$. Figure 8 shows the relation between the saturation magnetization and the particle size. The magnetizations are larger than the bulk value of cobalt and increase with decreasing particle size. For the smallest particles, the saturation magnetization was about 200 emu/g, about 20% larger than the bulk value of fcc cobalt, which is
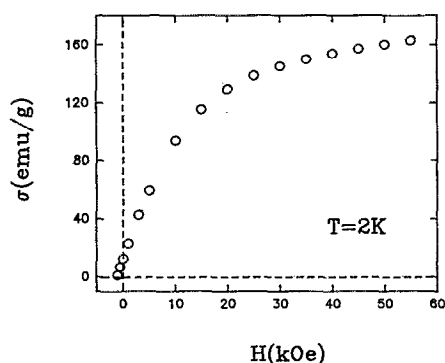

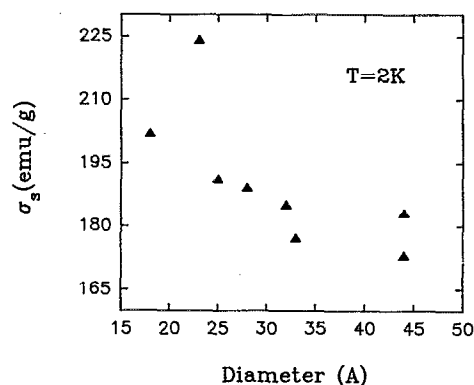FIG. 7. Magnetization as a function of field at 2 K for a sample with the average particle size of 3.3 nm.

FIG. 8. Saturation magnetization of Co particles at $T=2$ K (bulk $\sigma_s=166$ emu/g).

166 emu/g.[7] An enhancement of the magnetic moment per atom in cobalt has been observed in free cobalt clusters[8] and ultrathin Co/Ag(001) films,[9] and has been predicted by theoretical calculations[10,11] this is the first time that the enhancement has been observed in supported cobalt particles.

IV. CONCLUSIONS

We have successfully made cobalt fine particles with the size varying from 1.8 to 4.4 nm. The Co particles are single-domain particles and in superparamagnetic state at room temperature. The anisotropy constants in our Co particles are larger than that of bulk material. An enhanced magnetic moment per Co atom compared to the bulk was observed. This enhancement increases with decreasing size to be ~20% greater than bulk for 1.8 nm particles. This result is consistent with theoretical calculations and experimental results in free cobalt clusters.

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