Fabrication of $SmCo_5$ Alloy Magnetic Nanoparticles by Assistance of Copper and Their Magnetic Properties

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$SmCo_5$ magnetic nanoparticles were preparaed through a simultaneous reduction of $Sm(acac)_3 \cdot xH_2O$ and $Co(acac)_3$ by assistance of $Cu(acac)_2$ and $NaBH_4$ in the presence of oleic acid and oleylamine as a protectant. Supplementation of Cu activated the formation of $SmCo_5$ nanoparticles having a $CaCu_5$ structure, and use of $NaBH_4$ as a reducing agent played an important role to prevent samarium and cobalt from oxidation during preparation. The mean particle diameter was 3.4 nm, having a well-controlled crystal morphology. The magnetic properties of the prepared nanoparticles represented sufficiently high coercivity and magnetization of 1300 Oe and 15.7 emu g^{-1}, respectively, at room temperature.

$SmCo_5$ exhibits large coercivity, high magnetic anisotropy, and high Curie temperature.[1,2] Therefore, the fabrication of $SmCo_5$ nanoparticles has received much attention because of their potential use in various fields such as high-density data storage media and biotechnological applications.[3,4] Much research has already proposed fabrication of $SmCo_5$ alloy nanomagnets by physical methods such as sputtering and vapor condensation.[5,6] On the contrary, only a few chemical synthesis approaches have been applied to prepare such magnetic nanoparticles by a so-called polyol process to reduce samarium acetylacetonate with the thermal decomposition of cobalt carbonyl,[7–10] although there have been many attempts to fabricate ferromagnetic FePt nanoparticles by chemical synthesis.[11–13] However, the proposed polyol process uses harmful cobalt carbonyl as the sources of cobalt and also has a problem in that Sm^{III} ions cannot completely be reduced by this method and are easily oxidized to Sm_2O_3 in the experimental procedure. Therefore, none of the products reached high coercivity at room temperature. To solve this problem, Sun et al. have introduced metallic Ca to reduce Sm_2O_3 to Sm with sufficiently high temperature at 900 °C.[14,15] The product has shown high coercivity of 8 kOe at room temperature. However, the particles sintered and could not be controlled at a single nanometer order.

In a previous report, we showed that the addition of a third element such as gold and silver to magnetic nanoparticles during synthesis decreased the phase-transfer temperature to a ferromagnetic crystal structure and also improved the magnetic properties.[16,17] In this paper, we used copper, allied to gold and silver in the periodic table and comparatively inexpensive, in hope of the above-mentioned effects. In addition, we used sodium borohydride ($NaBH_4$), helping to reduce metal ions completely and preventing Sm and Co atoms from oxidizing, which is obviously important to obtain $SmCo_5$ alloys with high coercivity and magnetization at room temperature. The procedure is based on an improved nanoparticle-catalyzed polyol method assisted by hydride using $NaBH_4$ and Cu as a reducing agent and a promoter, respectively, to form a $CaCu_5$ crystal structure. Briefly, metal salts $Sm(acac)_3 \cdot xH_2O$ (0.33 mmol), $Co(acac)_3$ (1.67 mmol), $Cu(acac)_2$ (0.02 mmol), and a 1,2-hexadecanediol (4 mmol) were dissolved in 40 mL of dioctyl ether. The mixture was then heated with a mantle heater under stirring. Oleic acid and oleylamine (3 mmol each) as protectants were added immediately when the solution temperature reached 100 °C. All processes were carried out under a nitrogen atmosphere. After the solution was heated at 200 °C for 1 h, the reaction mixture was cooled down to room temperature for further addition of a strong reducing agent $NaBH_4$ (6 mmol). The solution was heated again under reflux at 280 °C for 1 h, giving a black dispersion.

Figure 1 represents the XRD patterns of products prepared with or without assistance of $Cu(acac)_2$ and/or $NaBH_4$. The powder preparaed with both $Cu(acac)_2$ and $NaBH_4$, shown in Figure 1a, was well in accordance with the $CaCu_5$ structure originating from $SmCo_5$ bulk. When prepared without $NaBH_4$ (Figure 1b), on the contrary, oxide peaks appear although the $CaCu_5$ structure is also observed. Moreover, the $CaCu_5$ structure could not be formed without assistance of $Cu(acac)_2$ and $NaBH_4$, and the produced nanoparticles were Co with a hexagonal structure (Data is not shown.). These results might indicate that Cu, produced immediately by reduction with the diol, accelerated the crystallization of Sm and Co to form alloy. Thus the nucleus of the alloy is formed under the first mild condition of the polyol process, and the successive reduction with the added strong reducing agent accelerates crystal growth of alloy nuclei at high temperature. Additionally, use of the strong reducing agent $NaBH_4$ leads to the considerable inhibition of particle oxidation, compared to that without it as shown in Figure 1b. Therefore, the use of both $Cu(acac)_2$ and $NaBH_4$ in the reduction of Sm and Co ions must be the key point for preparation of $SmCo_5$ by chemical

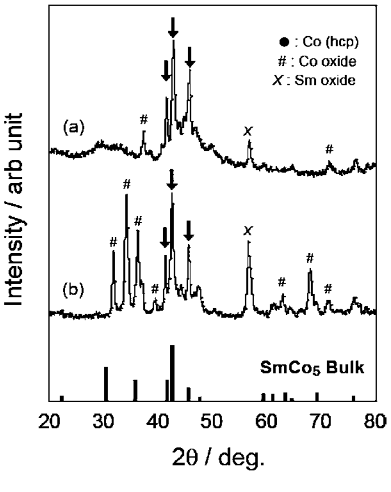

Figure 1. XRD patterns of nanoparticles chemically preparaed with assistance of Cu and $NaBH_4$ (a), and with Cu (b).

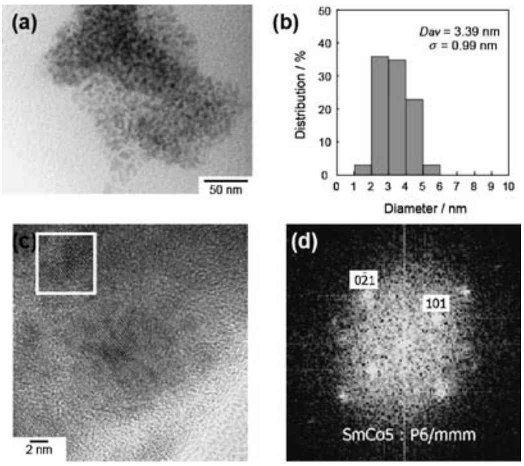

Figure 2. TEM image of the magnetic nanoparticles prepared in the presence of Cu and $NaBH_4$ (a), particles size distribution histograms (b), HR-TEM image of the magnetic nanoparticles (c), and FFT pattern corresponding to the rectangled area in (c), (d).

methods. Figure 2a shows TEM of the $SmCo_5$ nanoparticles produced with assistance of $Cu(acac)_2$ and $NaBH_4$. The mean particle size was 3.4 nm with a standard deviation of 0.99 nm (Figure 2b). The particles were a little bit aggregated with each other, which may be due to their magnetization. Moreover, the fast Fourier transform (FFT) pattern was consistent with (101) and (021) projections of a hcp structure due to $SmCo_5$ (Figures 2c and 2d). The elemental analysis of the particles revealed the composition of Sm, Co, and Cu as 1:5.6:0.06, indicating that almost all metal precursors could be reduced by added $NaBH_4$.

Magnetic properties of $SmCo_5$ nanoparticles were investigated with a SQUID magnetometer. Standard zero-field cooling (ZFC) and field cooling (FC) measurements vs. temperature as shown in Figure 3a gave a blocking temperature of ca. 350 K. It can be seen that the coercivity of the $SmCo_5$ nanoparticles reaches 1300 Oe at 300 K with saturated magnetization of 15.7 emu g^{-1} by the hysteresis loop (Figure 3b). The $SmCo_5$ nanoparticles with mean diameter of 6.9 nm represented relatively high coercivity of 1500 Oe at 300 K.[17] Even if the particle size was diminished by half, the coercivity of the particle was not significantly decreased and showed sufficient magnetic properties. On the other hand, the coercivity of the powder obtained without $NaBH_4$ dramatically decreased due to particle oxidation ($H_c = 300\,Oe$, $M_s = 24\,emu\,g^{-1}$), suggesting the substantial effect of the strong reducing agent to reduce Sm and Co ions to corresponding metals and to prevent Sm and Co metals from oxidizing. The coercivities of powder prepared with assistance of other third materials, such as palladium, platinum, nickel, and ruthenium, were also larger than that made without the third metal. Basically, metals other than copper produce similar effects, but the increment was less than that observed in the case of Cu. It can be assumed that the supplementation of the third metal decreases the phase-transfer temperature to the ferromagnetic crystal structure, coming to accelerate the crystallization to form the $CaCu_5$ structure, which results in high coercivity and magnetization at room temperature.[16,17]

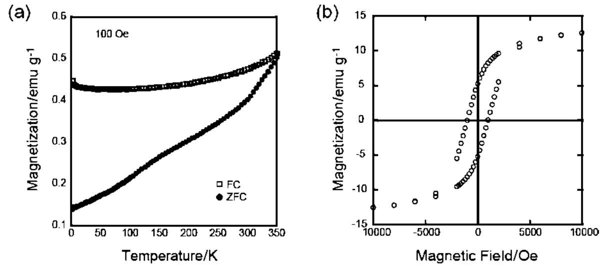

Figure 3. Magnetic properties of prepared nanoparticles; ZFC and FC vs. temperature hysteresis (a) and applied magnetic-field dependence of the magnetization of prepared nanoparticles at 300 K (b).

In summary, we have developed a novel procedure to make $SmCo_5$ magnetic nanoparticles by simultaneous reduction of metallic salts with assistance of Cu and $NaBH_4$. The nanoparticles have well-controlled crystal morphology, and their magnetic coercivity can be as high as 1300 Oe at room temperature. The third element of Cu plays an important role to catalyze the reduction of Sm and Co ions to form the $CaCu_5$ structure, while supplementation of $NaBH_4$ gives a quick reduction of Sm and Co ions and prevents the metals from oxidizing, leading to high coercivity and magnetization.

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