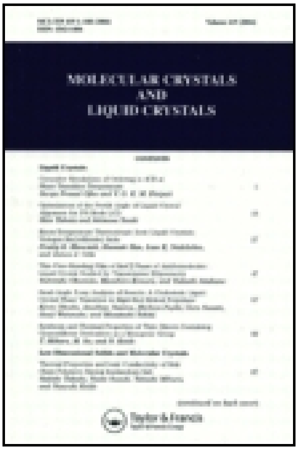

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The magnetic nanoparticle of SmCo was synthesized as thermal decomposition of metal salt by using pyrex bottle in the furnace. The magnetic properties of SmCo-nanoparticle were compared according to the ratio of Sm and Co component. The size of nanoparticle was confirmed by transmission electron microscopy (TEM) and scanning electron microscopy images (SEM). The crystal structure of nanoparticle was characterized by X-ray diffraction pattern (XRD). The magnetic properties were characterized with saturation magnetization from hysteresis loop by vibrating sample magnetometer (VSM).

Keywords: magnetic nanoparticle; SmCo; thermal decomposition

INTRODUCTION

For many years, magnetic material nanoparticles have been investigated because of their unique properties compared with bulk material

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and continuous broadening of the area of application of new magnetic material [1,2]. Fine ferromagnetic metal particles for high density recording media, precious metals or copper particles for conductive inks and pastes used in the electronic industry, cobalt powder used in cemented carbide industry to make hard materials by metallurgy [3,4]. Several synthetic techniques have been applied to synthesize magnetic metal nanoparticles, including thermal decomposition [5], metal evaporation [6,7], sonochemical method [8], reduction of metal salts by borohydride derivatives [9–10], co-precipitation using microwave system [11] and chemical vapor condensation [12]. Many studies on nanoparticles have focused on the synthesis of uniform spherical forms and the control of their particle size [5,8,13–16]. In the chemical synthesis method, the size of nanoparticle is very important [17,18]. In this study, SmCo magnetic nanoparticle were synthesized by a new solventless synthesis by metal-oleate complex thermolysis under low pressure. The magnetic properties of SmCo nanoparticle were compared according to the ratio of Sm to Co component. This paper describes magnetic and structural properties of nano-sized SmCo nanoparticles.

EXPERIMENTALS

Materials

The preparations for SmCo nanoparticles were carried out under argon atomphere. Samarium chloride hexahydrate (99.99% +), cobalt chloride hexahydrate(98% +), sodium oleate(98% +) and cyclohexane(99.5% +) were purchased from Aldrich Chemical Co. and used without further purification. Samarium chloride hexahydrate and cobalt chloride hexahydrate were used as initial material. The distilled water was purged with argon gas for 1 hr before reaction.

Synthetic Method of Preparation for the Mixture of Sm-Oleate and Co-Oleate Complexes

To prepare the mixture of the Sm-oleate and Co-oleate complexes, 0.3648 g of $SmCl_3{\cdot}6H_2O$ (1 mmol) and 1.1897 g of $CoCl_2{\cdot}6H_2O$ (5 mmol) were dissolved in deoxygenated water (50 ml, argon gas bubbling for 30 min) and 5.1757 g of sodium oleate (17 mmol) was dissolved in deoxygenated water (250 ml, argon gas bubbling for 30 min). The molar ratio of the Sm-oleate complex to Co-oleate complex was fixed as a ratio of one to five. The metal solution was added into a sodium oleate solution drop by drop under vigorous stirring for 30 min. The precipitate was separated by filtration and washed with distilled water to remove sodium and chloride ions. After drying perfectly, the mixture of the Sm-oleate and Co-oleate complexes was put into the pyrex tube. The complex in the pyrex tube was flushed with argon gas first, and then the tube was sealed at low pressure (0.8 torr).

The Process of Annealing for SmCo Nanoparticles

The sample was slowly heated up to 400°C by 1°C/min. After reaching the desired temperature, it was held at 400°C for 3 hrs and cooled to room temperature. The complex color was changed to black. The black product was washed with chloroform to separate oleate and distilled water to remove the oleate and residue ions, then washed with acetone. The product was dried with argon gas and stored in cyclohexane. The compostion of the mixture of the Sm-oleate and Co-oleate complexes was analyzed by thermo gravimetric analyzer (TGA, Perkin Elemer model TGA-7). SmCo nanoparticles were characterized with various experiments. The size and shape of SmCo nanoparticles were confirmed by transmission electron microscopes (TEM, HITACHI H-7500). The structure of SmCo nanopaticles was obtained by X-ray powder diffraction (XRD, Philips X'pert-MPD System) with a Cu K_α radiation source ($\lambda = 0.154056$ nm). The componential analysis of SmCo nanoparticles was carried out by scanning electron microscope energy-dispersive X-ray microanalysis (SEM-EDX, HITACHI S-2400). The morphology of the particle was characterized by field emission scanning electron microscope (FE-SEM, JSM-6700F). The magnetic properties were confirmed by vibrating sample magnetometer (VSM, Lake Shore 7300).

RESULTS AND DISCUSSION

Thermal Characterization of the Mixture of the Sm-Oleate and Co-Oleate Complexes

In our former study, metal-oleate complex was refluxed in solution such as dioctyl ether and also 3d transition metal nanoparticle was researched [12]. In this study we investigate preparation of nanoparticle by new solventless thermal decomposition. The thermal decompositon temperature of the SmCo-oleate complexe was studied by TGA analysis. The sample was heated from 50°C to 800°C. Figure 1 shows the thermogravimetric analysis data for the mixture of the Sm-oleate and Co-oleate complexes by heating. A strong endothermic peak for SmCo-oleate complex was obtained at 413°C and 471°C. The

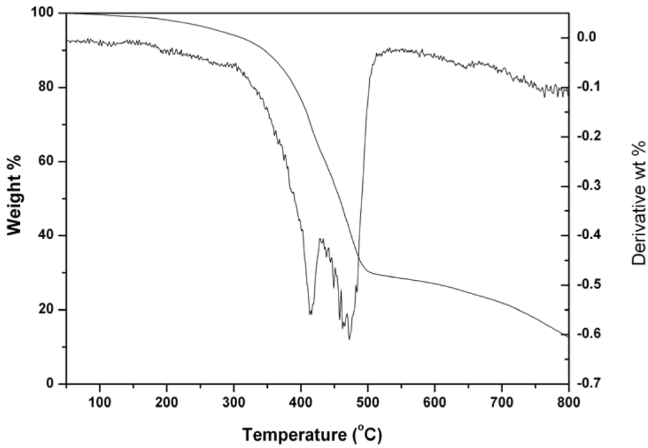

FIGURE 1 Thermogravimetric analysis data of the mixture of the Sm-oleate and Co-oleate complexes during heat treatment.

peak indicates the decompostion of oleate molecule of the mixture of the Sm-oleate and Co-oleate complexes according to the increase of temperature.

Characterization of SmCo Nanoparticles by Thermal Decomposition

TEM micrographs of SmCo nanoparticles (Fig. 2) were obtained with different molar ratio of Sm and Co contents. TEM sample was prepared when a drop of the nanoparticle iso-octane solution was carefully placed on the grid and dried in air. The sizes of SmCo nanoparticles were determined as about (a) 44 nm (b) 40 nm and (c) 43 nm. Most of the SmCo and Co nanoparticles are spherical. In the previous report, to prepare SmCo particle, the particles have been fabricated with various kinds of methods like sintered magnet, sputtered magnet, magnet by HDDR process and so on [20–23]. In those processes, it has a difficulty in obtaining magnetic nanosized-particle.

FE-SEM micrographs reveal the particle size and morphology of SmCo nanoparticles as Figure 3 shows the XRD patterns of the SmCo nanoparticles. The Co component was more reducible itself easily by the thermal decomposition than Sm component. Due to this reasons, a strong Co peak was detected in all samples. Although absolute intensity of all the peaks of Co was higher than the peak of the SmCo nanoparticles; as Sm contents increase, the peak of the SmCo nanoparticles is shown definitely.

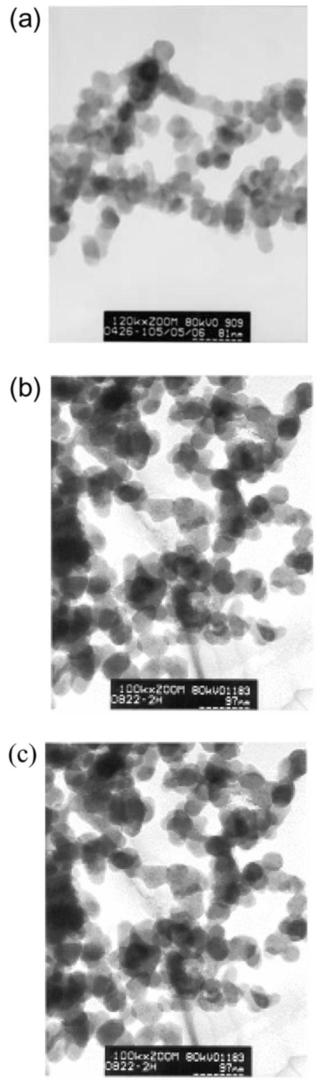

FIGURE 2 TEM images of SmCo nanoparticles synthesized by solventless thermal decomposition (a) SmCo nanoparticle annealed at 350°C for 3 hrs (Sm: 2.32%) (a), (b) SmCo nanoparticle annealed at 400°C for 2 hrs (Sm: 13.54%) and (c) SmCo nanoparticles annealed at 400°C for 3 hrs (Sm: 17.80%).

FE-SEM micrographs are revealing the paticle size and morphology of SmCo nanoparticles as Figure 4(a)–(c), which explain about morphology according to reaction temperature. The average size of SmCo

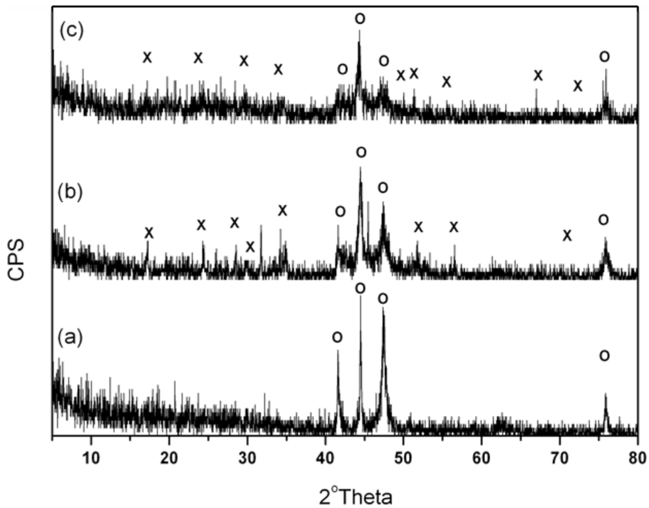

FIGURE 3 X-ray diffractograms of SmCo nanoparticles with the different molar ratio of Sm and Co contents (a) SmCo nanoparticles (Sm: 2.32%), (b) Sm-Co nanoparticles (Sm: 13.54%) and (c) SmCo nanoparticles (Sm: 17.80%).

nanoparticles that has the low Sm contents was determined to be about 2 μm (Fig. 4(a)). The increase in SmCo particle size with increasing Sm contents is quite obvious in the microscope (Fig. 4(b) and (c)). This value should be also compared with the average grain size for SmCo magnetic particles of ~10 m in the previous study [24].

SEM-EDS analysis (Fig. 5) was carried out by an electron beams (200 kV) to investigate the contents of the SmCo nanoparticles. EDX data of Figure 5 indicate 2.32% of Sm and 97.68% of cobalt. Figure 5(b) and (c) indicate, in order, the contents of Sm and Co are (b) 13.54%, 86.46%, (c) Sm 17.80%, Co 82.20%, respectively. Figure 5 indicates that there is no impurity except the cobalt and samarium component. Washing the product sufficiently is necessary to obtain pure product to remove Na and Cl ions.

Magnetic Properties of SmCo Nanoparticle

The saturation magnetization (Ms) of the magnetic applied 15 kOe field. Figure 6 shows the hysteresis loops of SmCo and Co nanoparticle powders to characterize magnetic properties at the room temperature. The value of saturation magnetization and coercivity are (a) 157.31 emu/g and 223 Oe (Sm:2.32%), (b) 104.7 emu/g, 243 Oe

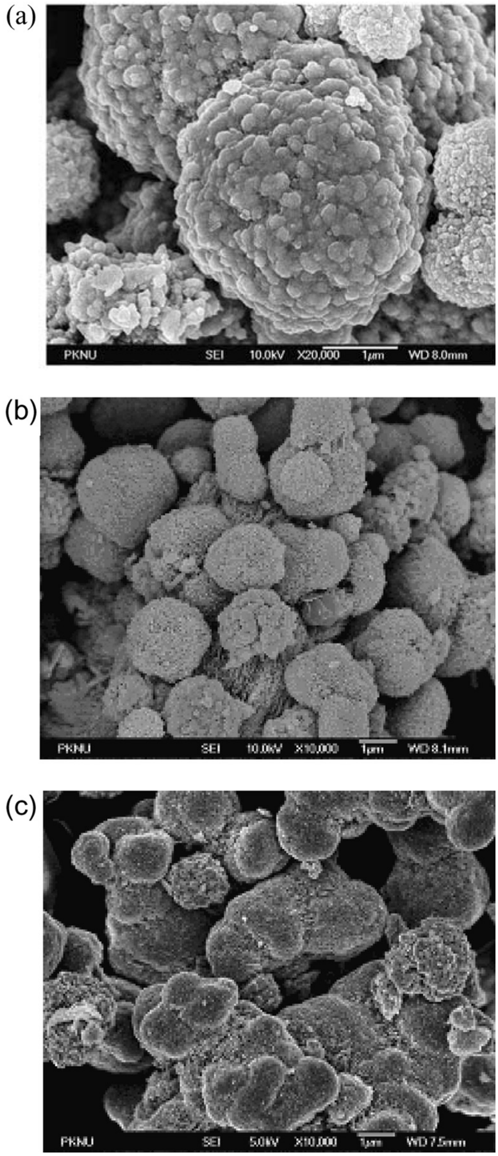

FIGURE 4 The FE-SEM images of SmCo nanoparticle according to the molar ratio of Sm to Co contents: (a) SmCo nanoparticles (Sm: 2.32%), (b) SmCo nanoparticles (Sm: 13.54%) and (c) SmCo nanoparticle (Sm: 17.80%).

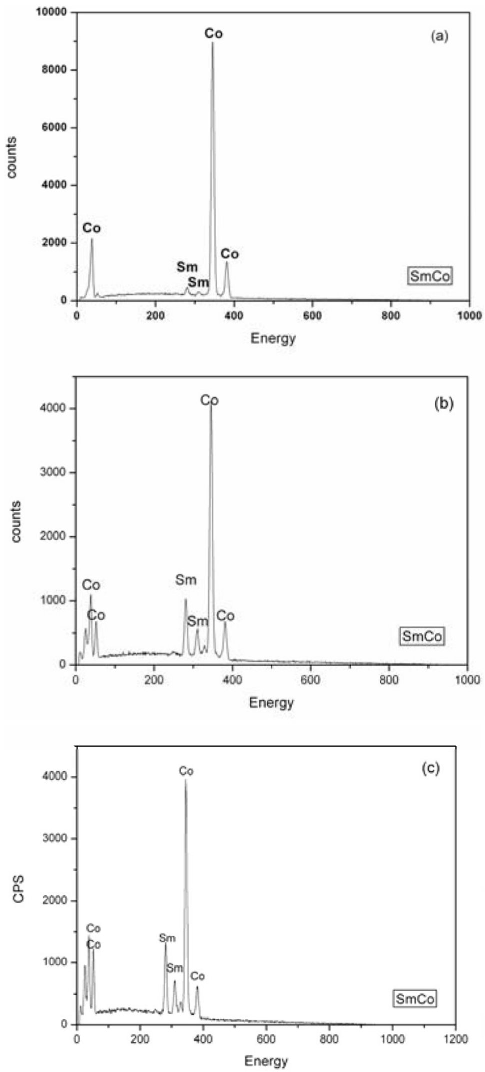

FIGURE 5 SEM-EDS data of SmCo nanoparticles: (a) SmCo nanoparticles (Sm: 2.32%), (b) SmCo nanoparticles (Sm: 13.54%) and (c) SmCo nanoparticles (Sm: 17.80%).

(Sm:13.54%), (c) 78 emu/g , 930 Oe (Sm:17.80%) of SmCo nanoparticle, respectively. The increase of coercivity is resulted from the increase of Sm content of samples. The salient point of difference

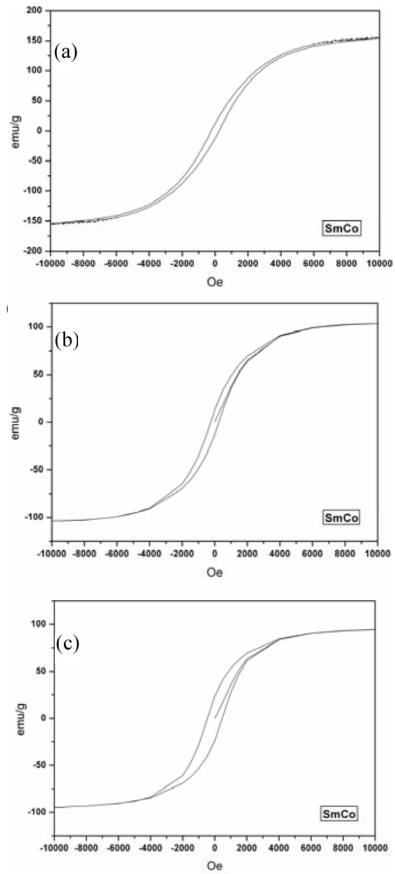

FIGURE 6 The hysteresis loops of the SmCo nanoparticles: (a) SmCo nanoparticles (Sm: 2.32%), (b) SmCo nanoparticles (Sm: 13.54%) and (c) SmCo nanoparticles (Sm: 17.80%).

between previous study and ours is to control the size of SmCo nanoparticle and to get nano-sized spherical shape [24]. Generally, the coercivity of the fine particles is found to depend on particle size, and the higher value is realized when the particles have a single domain structure. In this study, the maximum coercivity, 458 Oe, was obtained when the mean diameter of the particles was about 50 nm. The rare earth metal nanoparticle is useful to prepare exchange-coupled magnet through nanocomposition between hard and soft magnetic nanoparticles [25].

TABLE 1 A Summary Table for the Dependence of Nanoparticle Size, Saturation Magnetization and Coercivity as Function of the Molar Ratio of the Sm Contents

Sm contents	2.32%	13.54%	17.8%
Particle size (nm)	44	40	43
Saturation Magnetization (emu/g)	157.31	104.7	78
Coercivity (Oe)	223	243	930

CONCLUSIONS

The SmCo nanoparticles were synthesized by thermal decomposition method that is a new solventless synthesis by thermolysis of metal-oleate complex under low pressure (0.8 torr). The summary provides the dependence of nanoparticle size, saturation magnetization and coercivity as function of the molar ratio of the Sm contents in Table 1. SmCo magnetic nanoparticles were obtained as uniform size of 40 nm, more or less. Moreover, the increase in SmCo particle size is quite obvious with increasing Sm contents due to disposition of SmCo alloy to form hexagonal shape. and the SmCo nanoparticle that has high Sm contents (17.80%) shows the highest coercivity of 930 Oe with saturation magnetization of 78 emu/g.

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