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Heating Temperature Effect on the Magnetic Property of α-Fe Nanoparticle

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The effect of heating temperature on the magnetic property of α-Fe nanoparticle produced by thermal decomposition method has been investigated. The Fe^{2+}-$oleate_2$ ligand complex was annealed at 400°C in pyrex tube under 10^{-2} torr for 2 hrs, and then reduced at a different temperatures under $Ar + 4\%$ H_2 mixture gas atmosphere. The magnetic property of α-Fe nanocrystallite was affected with the different heating temperatures. The structure and properties of prepared α-Fe nanoparticle was characterized by TGA, XRD, TEM, and VSM.

Keywords: α-Fe nanocrystallite; soft magnetic; thermal decomposition

INTRODUCTION

Many methods to make nanoparticles of either pure metal or metal oxides have been reported in the literature since then [1,2]. These inorganic nanoparticles have recently attracted interests, because of their expected chemical and physical properties resulting from their size. These interests in the properties of objects have required for the control of the monodispersity, size, shape and the nature of the chemical species present at the surface. This concerns the fields of optics, electronics and magnetic, and magnetic nanomaterial [3,4], the development of size controlled nanoparticles became a very

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important issue in their application to high performance permanent magnets [5], targeted delivery of drugs [6], ultra-high density magnetic storage device [7]. When magnetic nanoparticles are prepared, particle aggregation due to their magnetism and Van der Waals attraction leads to unwanted growth of nanoparticles. Nanoparticles are difficult to disperse them from each other. In addition, there are other problems associated with metallic nanoparticle such as oxidation and growth in particle size. Several synthetic approaches including the thermal decomposition [8], coprecipitation of metal salts in aqueous solution [9], high-temperature reduction of metal salts [10] and reduction inside reverse micelles are useful method to solve these problems. But the magnetic nanomaterials synthesized by surfactant did not generally exhibit the excellent magnetic property like that of bulk magnetic material because of the pinning phenomenon of the α-Fe surface spins by surfactant coated on the surface of the magnetic nanoparticle [11]. In this experiment, the effect of heating temperature on α-Fe nanoparticles was investigated for the changed magnetization and size.

EXPERIMENTAL

Materials

Fe^{2+}-oleate$_2$ complexes were prepared from $FeCl_2 \cdot 4H_2O$ (99+ %), and Na-oleate ($C_{17}H_{33}COONa$, 98%). They are purchased from Aldrich. High purity Ar gas (99.999+ %) was used for purging the distilled water and to prevent the oxidation of the prepared nanoparticle. To wash the as-annealed nanoparticles using pyrex tube, chloroform (99.5%) and methanol (99.75%) were obtained from Junsei Chemical Co. An Ar+ 4% H_2 mixture gas (99.99%) was flowed to reduce the Fe_3O_4 nanoparticles.

Preparation of α-Fe Nanoparticles

The Fe^{2+}-oleate$_2$ complex was synthesized from $FeCl_2 \cdot 4H_2O$ and Na-oleate. 6 g of $FeCl_2 \cdot 4H_2O$ (30 mmol) and 18.27 g of Na-oleate (60 mmol) were dissolved in mixture solvent composed with hexane (105 mL), distilled water (45 mL) and ethanol (60 mL). They were heated at 60°C for 2 hrs. After cooled to room temperature, it was washed with distilled water. Prepared iron solution was transferred to pyrex tube and dried for two day. Dried Fe^{2+}-oleate$_2$ complex was sealed at the 10^{-2} torr and the tube was heated from room temperature to 400°C at 1°C/min. The pyrex tube was kept at 400°C for 2 hrs, and cooled to room

temperature. To remove the decomposed oleate coated on the surface of as-annealed nanoparticles, black samples were centrifuged [8]. And then, prepared nanoparticle were reduced at 600°C, 700°C, 750°C and 800°C for 30 min under Ar + 4% H_2 mixture gas atmosphere, obtained α-Fe nanoparticle was stored in cyclohexane to keep from oxidizing.

Characterization

The thermal property of the as-synthesized Fe^{2+}-$oleate_2$ complexes and prepared nanoparticles was analyzed by thermo gravimetric analysis (TGA). And the structure and morphology of the prepared particles were investigated using an x-ray powder diffraction (XRD) with a Philips X' pert-MPD System with monochromated a Cu-Kα radiation source ($\lambda = 0.154056$ mm) and transmission electron microscopy (TEM) with HITACHIH-7500 TEM. The magnetic properties such as saturation magnetization and coercivity were measured by Lake Shore 7300 vibrating sample magnetometer (VSM) with applied field up to 12 kOe.

RESULTS AND DISCUSSION

The stabilization of magnetic nanoparticles can be achieved by surfactant as oleate. The decomposition of $FeCl_2$ in the presence of long

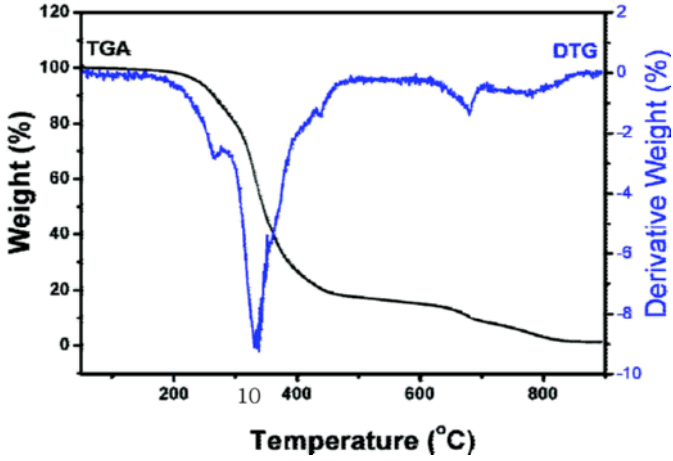

FIGURE 1 TGA curve of Fe^{2+}-$oleate_2$ complexes.

chain surfactant yield Fe_3O_4 nanoparticles of controlled size, shape and therefore magnetic properties, and over 600°C in the presence of H_2, these particles were converted into α-Fe nanoparticle. We successfully synthesized α-Fe nanoparticles through reducing with $Ar + 4\%$ H_2 mixture gas by thermal decomposition method. The decomposition temperature of Fe^{2+}-oleate$_2$ complexes was confirmed by TGA data, and it is shown in Figure 1. There are two weight loss steps in the temperature range of 200–450°C and 600–800°C. The weight loss at 200–450°C (81.79%) is attributed to the decomposition of physically adsorbed oleates and the decomposition of the oleate chain, whereas that at 600–800°C (16.62%) ascribed to the decomposition of strongly bonded oleates coated on the Fe nanoparticles [12]. The weight loss stopped at 844°C. Reducing temperatures to make the α-Fe nanoparticles at 600°C, 700°C, 750°C, and 800°C were decided from TGA data. When prepared nanoparticles were annealed at 600°C, it was the size about 20 nm and square shape (Fig. 2(a)). However, as heating

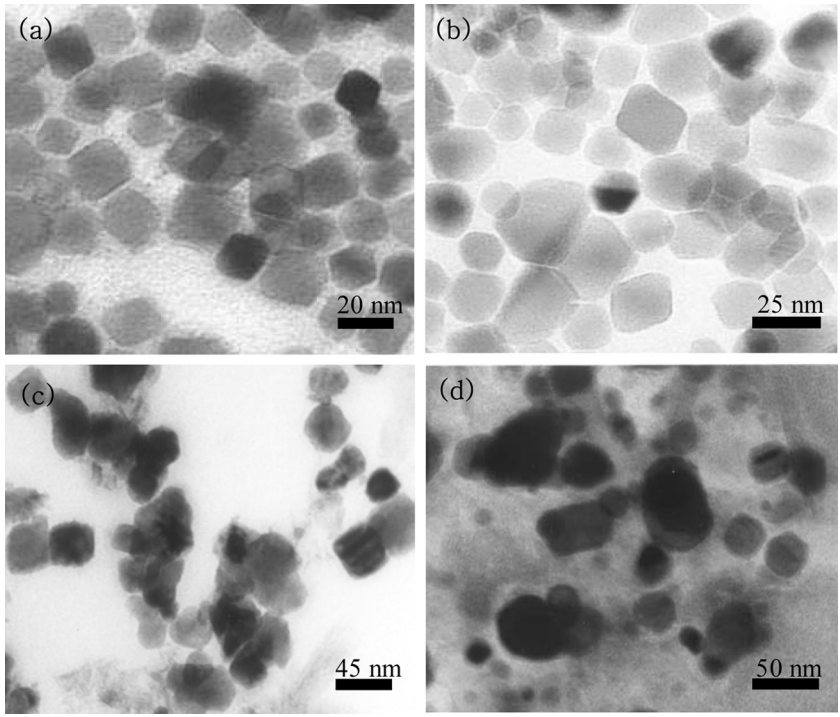

FIGURE 2 TEM images of α-Fe nanoparticles with different reducing temperatures; (a) 600°C, (b) 700°C, (c) 750°C and (d) 800°C.

temperature increased from 700°C to 750°C, the size of prepared nanoparticle grew from 25 to 40 nm. Therefore, size distribution was wide. As shown in Figures 2(b) and (c), after annealing at 800°C, the particle size of prepared α-Fe nanoparticles ranges from 20 nm to 70 nm with the mean diameter of about 47 nm, and they show the irregular shape as shown in Figure 2(d). The difference of particle size between each nanoparticles annealed in various temperatures is attributed to the fact that increasing temperature lead to grow nanoparticles by coalescence during the reducing process. The XRD patterns of α-Fe nanoparticles reduced at 600°C (a), 700°C (b), 750°C (c) and 800°C (d) for 30 min are shown in Figure 3. The discernible peaks in this figure can be indexed to (110) and (200) planes of cubic unit cell, which corresponds to that of α-Fe structure (JCPDS card No.06–0696). In this figure, calculated sizes of prepared α-Fe nanoparticles by Debye Scherrer equation are (a) 19.56 nm, (b) 25.66 nm, (c) 38.40 nm and (d) 44.85 nm. This result is agreed with TEM observation. Figure 4 displays hysteresis loop of α-Fe nanocrystals by VSM at room temperature. As you see in this figure, when external magnetic filed is applied at 12 kOe, these α-Fe nanoparticles were not saturated. But, from this measured data, the trend about magnetic properties can be confirmed. When heating temperature was increased form 600°C to 800°C, we could obtain the magnetization value at (a) 140.63 emu/g,

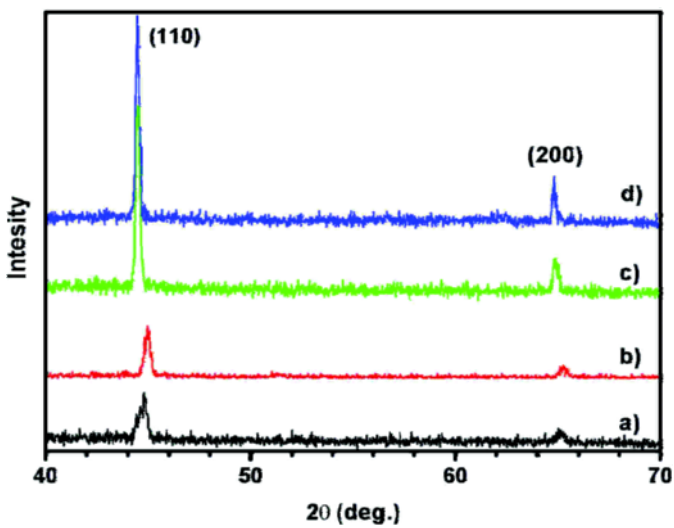

FIGURE 3 XRD patterns of α-Fe nanoparticles different reducing temperatures; (a) 600°C, (b) 700°C, (c) 750°C and (d) 800°C.

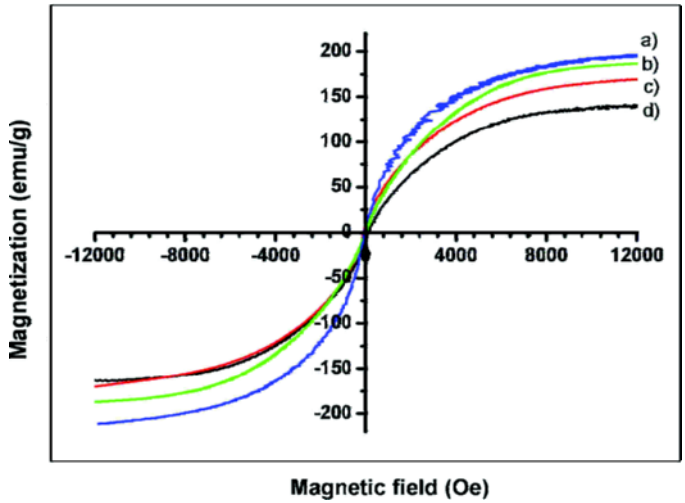

FIGURE 4 VSM curve of α-Fe nanoparticles different reducing temperatures; (a) 800°C, (b) 750°C, (c) 700°C and (d) 600°C.

(b) 169.79 emu/g, (c) 186.59 emu/g, and (d) 196.08 emu/g with maximum external field at 12 kOe. The increased heating temperature lead to the enhanced magnetization value, but these values are lower than that of bulk α-Fe ($M_{bulk} = 213$ emu/g) [7]. When α-Fe nanoparticles were produced by thermal decomposition from Fe^{2+}-$oleate_2$ complexes, α-Fe nanoparticle show the low magnetic property by the behavior of spin pinning by the interaction between the organic surfactant and the surface spins of nanoparticles [11]. However after annealed over 600°C, the particle size and the magnetic property were gradually increased through the decline of surface area by increasing size and decomposition of organic surfactant.

CONCLUSIONS

α-Fe nanoparticles with different reducing temperatures were prepared by the thermal decomposition method. We found that the heating temperature plays a critical role in the size and magnetic properties of α-Fe nanoparticles. When the reducing temperature is increased from 600°C to 800°C, magnetic saturation is increased from 140.63 emu/g to 196.08 emu/g. The results reported here lead to index for thermal decomposition method whose study is under progress.

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