Microstructure and Magnetic Properties of Fe Nanoparticles Synthesized by Chemical Vapor Condensation

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Nano-sized Fe particles were synthesized by Chemical Vapor Condensation (CVC) using the precursor of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) as the source under a flowing helium atmosphere. The effect of CVC processing parameters on the formation of nanoparticles was studied. Microstructures and magnetic states were investigated systematically by means of XRD, HRTEM, DTA-TGA, Mössbauer spectroscopy and VSM. We synthesized the nanoparticles with nearly spherical shape, core-shell type structure and 5–13 nm in mean size by using liquid nitrogen cooling. Average particle size increased with increasing the decomposition temperature of the precursor. The magnetic states of Fe nanoparticles changed from ferromagnetism to superparamagnetism with the particle size and microstructure. The effect of particle size on the saturation magnetization and coercivity of nanoparticles were also discussed.

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1. Introduction

Nanomaterials have recently become one of the most active research fields in the areas of solid state physics, chemistry, and materials science.^{1,2)} The study of the magnetic properties of fine particles has been traditionally urged by both a technological and theoretical interest connected with the possibility of developing a better understanding of magnetic phenomena related to size effect.

Various physical, chemical and mechanical methods have been developed in recent years for the synthesis of nanoparticles.³⁾ The main characteristics of Chemical Vapor Condensation process of this study are the thermal decomposition of metalorganic precursors and evaporation/condensation of volatile species in a reduced pressure condition. High energy sources such as a focused laser beam, combustion flame or plasma torch have been used for the thermal decomposition of metalorganic reagents.^{4,5)} These processes have been applied successfully to the production of commercial quantities of various kinds of nanoparticles. However, the synthesized powders have a tendency of the highly agglomerated state. To overcome the nanoparticle agglomeration problem, the Inert Gas Condensation (IGC) method was introduced in late 1980.⁶⁾ The loose agglomerated nanoparticles with uniform size and high purity can be synthesized by this method, but it has a limitation of scaling-up and evaporation problem of low vapor pressure materials.

In the present study, we have taken the Chemical Vapor Condensation (CVC) process, which combine the ability to synthesize non-agglomerated powders by the IGC process with the high rate of production capability of the flame and plasma processes.⁷⁾ A wide range of precursors is available commercially in CVC process, thus it has an advantage applicable to almost all materials and can usually produce a large amount of nanoparticles with a non-agglomerated state.

In this paper, Fe nanoparticles were synthesized by Chemical Vapor Condensation (CVC) method from organometallic precursor of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$). The structural and

magnetic properties of free-standing particles were discussed.

2. Experimental Details

The principle of CVC process was exhaustively described in the previous works.^{7,8)} The precursor of $\text{Fe}(\text{CO})_5$ was decomposed in a heated furnace and condensed into particles that deposited upon the rotating liquid nitrogen cooled finger. Thus produced Fe powders were scraped off and collected. The morphologies and lattice images of particles were determined with High Resolution Transmission Electron Microscopy (HRTEM). Identification of the phases in the samples was carried out in x-ray diffractometer with CuK_α radiation. Magnetic characterization of the samples was made using vibrating sample magnetometer (VSM) at room temperature by saturating the sample in a field of 21.6 MA/m. Mössbauer absorption spectra were recorded with a conventional constant acceleration spectrometer using a ^{57}Fe source at room temperature. The average particle size of each sample was determined by BET method assuming a spherical shape. TG-DTA of the Fe nanoparticles was conducted in air at a heating rate of 10°C/min.

3. Results and Discussion

Spherical particles of different sizes within the nanometer range and very uniform in size and shape were obtained by CVC process. During the fabrication process, the precursor of $\text{Fe}(\text{CO})_5$ can be easily transported into a bubbler by a micro-pump due to its liquid state at room temperature. Vaporization of liquid $\text{Fe}(\text{CO})_5$ was realized in the bubbler at 150°C and subsequently passed into the heated furnace by carrier gas of helium for a decomposition. The minimum of the decomposition temperature for $\text{Fe}(\text{CO})_5$ is about 350°C. Magnetic Fe particles can form intricate long strands when they agglomerate to minimize the magnetic energy. HRTEM (Fig. 1) shows the typical morphology and lattice image of the CVC-prepared Fe nanoparticles. The particle shape is nearly

Fig. 1 Typical HRTEM micrograph of Fe nanoparticles.

spherical with a core-shell type structure. The core is metallic Fe and the shell is composed of Fe_3O_4 .

The characteristics of finally formed particles are affected by the preparation parameters, such as the flow rate of carrier gas, gas pressure in work chamber, heating temperature for vaporization of precursor, kinds of inert gases, decomposition temperature for precursor vapor, condensing temperature, *etc.* Among above factors, decomposition temperature of precursor at the tubular furnace plays an important role on the size of particle. To investigate the effect of decomposition temperature on particle size, several particle samples were synthesized at various pyrolytic temperatures from 400 to 1100°C, meanwhile, other preparation conditions were kept the same. Figure 2 illustrates XRD patterns of the samples formed at different decomposition temperatures, respectively. It is shown that no visible diffraction peaks of Fe are found for the samples prepared at the decomposition temperature below 900°C. The intensity of Fe peaks increase with increasing decomposition temperature above 900°C.

The relationship between decomposition temperature and particle size is well exhibited in Fig. 3. The particle size was evaluated from BET measurements. It is indicated that the mean size of Fe nanoparticles increases with increasing the decomposition temperatures. During the decomposition of precursor vapor in the heated furnace, nuclei are formed and grown to form the observable particles. A saturation vapor pressure ratio increases with an increase of the decomposition temperature. It is believed that higher saturation vapor pressure ratio enhances the growth of nucleus, which results in the larger particle formation.

TG-DTA curves for typical Fe nanoparticles were recorded in air at a heating rate of 10°C/min as shown in Fig. 4. By thermal analysis of the oxidization behavior of nanoparticles, it is further confirmed that the microstructure of Fe nanoparticles consist of the core-shell structure. In a heated air atmosphere, it is expected that the active crystallite Fe core is transformed to oxide and the oxide shell is further converted to

Fig. 2 X-ray diffraction patterns of Fe nanoparticles synthesized at temperatures from 400 to 1100°C. All samples were collected from liquid nitrogen cooled chiller. The carrier gas is helium.

Fig. 3 Dependence of decomposition temperature of $\text{Fe}(\text{CO})_5$ precursor on Fe nanoparticle size.

more stable one. On the DTA curves, three exothermal peaks are displayed at temperatures near to 77, 170 and 260°C, respectively. The exothermal peak at 77°C associated a weight loss is attributed to release of absorbed gases or moisture on the surface of particles. The exothermal peak at 170°C accompanied with a weight gain is recognized to a chemical reaction in which the crystal Fe core is oxidized to Fe_3O_4 . Further transformation of Fe_3O_4 to Fe_2O_3 accounts for the occurrence of the exothermal peak at 260°C. This is in good accordance with XRD results of Fe nanoparticles as prepared and heat treated at various temperatures (Fig. 5).

A Mössbauer study has been made on Fe nanoparticle samples (a)-(d) at room temperature. The preparation conditions for the samples are presented in Table 1. As shown in Fig. 6,

Table 1 Results of Mössbauer spectra, mean size and the preparation conditions for various Fe nanoparticles.

Samples	Core (α -Fe)		Shell (Fe_3O_4)		Super-paramagnetism (%)	Mean size (nm)	Preparation conditions		
	Bulk (%)	Middle (%)	Bulk (%)				Decomposition temperature	Carrier gas	Chiller temperature
(a)	0	0	0		100	5.4	400°C	He	-196°C
(b)	20	5	0		75	~ 7.0	1000°C	He	-196°C
(c)	34	24	21		21	10.3	1000°C	Ar + 1 vol%O ₂	-196°C
(d)	70	0	20		10	12.3	1000°C	He	25°C

Fig. 4 DTA-TGA curves for Fe nanoparticles recorded in air at a heating rate of 10°C/min.

Fig. 5 X-ray diffraction patterns of Fe nanoparticles as prepared and heat treated at temperatures of 250, 400 and 700°C.

a doublet peak, which is an evidence of superparamagnetism, composes the Mössbauer spectrum of sample (a). The sextet of Mössbauer spectrum occurs in other samples, which means a ferromagnetic state exists. It had been demonstrated

Fig. 6 Room temperature Mössbauer spectra for Fe nanoparticles: labels (a)–(d) correspond to samples (a)–(d).

from our previous work⁹⁾ that the core of particles in sample (a) is crystal Fe with around 5 nm in size, and the shell is amorphous-like matter. The fitted results of Mössbauer spectra on the four samples are displayed in Table 1, in which the item of “bulk” means the hyperfine fields in nanoparticles equal to that of corresponding bulk materials, and “middle” means a distribution of hyperfine field. It is shown that the variation of magnetic states, *i.e.* from superparamagnetism to ferromagnetism, can be realized by careful control of the preparation parameters.

Figure 7 shows the change in saturation magnetization with particle size for the passivated Fe nanoparticles. The reduction of saturation magnetization with decreasing size is expected because of the presence of surface oxides due to passivation, namely, the volume ratio of the oxides to metal becomes larger as particle size decreases. This result is in good agreement with that of Fe particles prepared by the inert gas evaporation method.¹⁰⁾ Figure 8 shows the variation of coercivity (H_c) of Fe particles with mean particle size. No strong size dependence of H_c is found.

Most of the metallic particles are protected by a thin oxide layer, and exhibit much lower values of magnetization than

Fig. 7 Variation of saturation magnetization with particle size of Fe nanoparticles at room temperature.

Fig. 8 Variation of coercivity with particle size of Fe nanoparticles at room temperature.

the bulk. The existence of magnetic dead layers as a source for the lower magnetization in these particles has now been ruled out. Magnetic hysteresis studies on fine particles show values of effective anisotropy and coercivity orders of magnitude higher than in the bulk. Such large anisotropy could arise from magnetic surface anisotropy, interface, and/or the magnetoelastic energies caused by stress/pinning induced by the lattice mismatch at the coated surface. The magnetic state of the surface oxide plays a very important role in the temper-

ature dependence of coercivity $H_c(T)$ of the whole particle. However, the hysteresis behavior of ultrafine particles is not explained consistently by any of the existing models.

The reason for no size dependence of H_c in this study is not clearly elucidated, but it is thought to be originated from the strong spin interaction between the core and shell, because the volume fraction of oxide shell is relatively large due to the nanometer size of the as-prepared particles.

4. Summary

Fe nanoparticles are successfully synthesized by the pyrolysis of iron pentacarbonyl through chemical vapor condensation method. In the CVC-prepared Fe nanoparticles, the core consists of crystal Fe and the shell composes of crystal Fe_3O_4 or amorphous-like matter. Mean size of Fe nanoparticles increases with increasing the decomposition temperature of the precursor vapor, because of higher saturation vapor pressure at higher decomposition temperature. The oxidation sequence of Fe nanoparticles can be confirmed that the transformation of Fe_3O_4 to Fe_2O_3 followed Fe core oxidation to Fe_3O_4 . By controlling the size and microstructure of Fe nanoparticles, their magnetic states can be changed from superparamagnetism to ferromagnetism. Saturation magnetization of Fe nanoparticles is a function of particle size. No distinct size dependence of H_c was found for CVC-prepared nanoparticles.

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