Aerosol Synthesis and Growth Mechanism of Magnetic Iron Nanoparticles

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Abstract. Magnetic oxide-coated iron nanoparticles with the mean size ranging from 6 to 75 nm were synthesized by aerosol method using iron carbonyl as a precursor under the flowing inert gas atmosphere. Oxide shells were formed by passivation of as-prepared iron particles. The influence of experimental parameters on the nanoparticles’ microstructure, phase composition and growth behavior as well as magnetic properties were investigated and discussed in this study.

Introduction

Synthesis and application of magnetic nanoparticles are emerging in wide areas, especially in electronics and biotechnology due to their special characteristics of superparamagnetic properties and single-domain magnetism. The magnetic properties of fine particles have been studied intensively with both technological and theoretical interest connected with magnetic phenomena related to size effect. Furthermore, this research field is in rapid progress because of wide potential application areas, such as components of magnetic tapes, ferrofluid, magnetic refrigerants, and the wide range of medical applications. A wide range of techniques to fabricate magnetic nanoparticles has been developed rapidly over the past decades, such as mechanical milling, spray drying, sol-gel, sonochemistry, etc. Among them, chemical synthesis of nanoparticles is a rapidly growing field, because of its versatile applicability to almost all materials and high rate of production capability with little agglomeration. In this study, the structure and magnetic properties of magnetite coated iron nanoparticles synthesized by Chemical Vapor Condensation (CVC) method were examined and discussed.

Experimental

The basic equipment for CVC process was described previously [1]. Liquid precursor was heated in the special bubbler, evaporated and transported by carrier gas flow to the preliminary heated tubular furnace for decomposition. Decomposition of the precursor can be controlled in tubular furnace as a heat source. Metallic vapor formed in tubular furnace was condensed in the vacuum chamber. The passivation process was performed with dosing inert gas with small amount of oxygen content before opening the chamber to air. Nanocrystalline iron particles piled up at the bottom and on the wall of the chamber were collected carefully. In this work, we use argon or helium as carrier gas and liquid iron carbonyl (Fe(CO)₅) as a precursor.

The phase analysis of samples was carried out on DRON-2.0 diffractometer with monochromatic CuKα radiation. The morphologies and particles size distribution were determined by transmission electron microscopy using TEM (JEOL, 2000FXII) equipment. The powder for TEM investigations was ultrasonically dispersed in ethanol and dropped on a carbon coated copper
grid. Morphology of the nanoparticles was analyzed with Jeol-840A SEM. Mössbauer study was achieved at room temperature (298K) by using $^{57}$Fe isotope as source of radiation. Metallic iron and iron oxides can be distinguished based on the magnitude of internal magnetic field and the magnitude of the shift of spectral centre [2]. To compare the ratio of metallic and oxide part, the areas of the respective Mössbauer subspectra were examined. Hysteresis loop of powder samples was measured by vibration sample magnetometry methods in the field of 10kOe.

The average particle size of each sample was calculated as the center of gravity from particles’ mass distribution. Firstly, the particle size distribution was calculated by measuring of diameters of 200-300 nanoparticles from TEM microphotographs.

**Results and discussion**

Fig. 1 shows TEM micrographs of oxide coated nanoparticles with the mean size of 8 and 28 nm. Electron diffraction patterns show the same phase composition of such particles, iron core and oxide shell. With the increase of reaction temperatures, the average size of the iron particles increased and the particle size distribution becomes wider and more asymmetrical with the size increment. Particles did not appear at the temperatures lower than 260°C. The shells consisted of magnetite [3] and their thickness was evaluated about 2-3nm. X-ray diffraction pattern didn’t show any additional phase except BCC iron. However, slight diffusive peaks which belonged to oxides were distinguished.

![TEM images and electron diffraction patterns of nanoparticles](image1)

Fig. 1. TEM images and electron diffraction patterns of nanoparticles with the mean size of (a) 8nm and (b) 28nm

Selected Mössbauer spectra are shown in the Fig. 2. It should be noticed that the effective Debye temperatures of iron atoms and oxides are generally different and this may give rise to experimental error, when basic determination on room temperature measurements is performed alone [2]. Mössbauer spectra of the large particles with the size of more than 19 nm showed sextet corresponding to Fe$^{0}$ atoms and small amount of magnetite (Fig. 2(c)). The “bulk” means the hyperfine fields in nanoparticles equal to that of corresponding bulk materials. Other states of Fe atoms were invisible.

![Mössbauer spectra of iron nanoparticles](image2)

Fig. 2. Mössbauer spectra of iron nanoparticles with the mean size of (a) 7nm, (b) 12nm, and (c) 21nm.
In the case of smallest nanoparticles (less than 7 nm) obtained in this experiment, an asymmetric doublet peak was shown in Mössbauer spectrum (Fig. 2(a)). There are no any atoms in Fe\(^0\) state in the ultra fine particles and spectra were evaluated to iron oxide and hydroxides. It implies that volume fraction of oxide shell was relatively high.

In the particles of mean size 10-19 nm, doublet peak corresponding to Fe\(^{3+}\) atoms and sextet of non-stoichiometric magnetite are observed. Mössbauer spectra of these samples measured in the room temperature showed the broad minimum, which can include non-crystalline magnetic phase and superparamagnetic iron. According to CVC parameters, particles’ structure contains about 15-100\% of bulk iron and up to 45\% of Fe\(_3\)O\(_4\), another phases can be Fe (Fine), α-FeOOH (Fine and middle), or γ-FeOOH.

Considering the content of oxide and iron phase in nanoparticles under the approximation of its spherical shape, we can geometrically calculate average core diameter and shell thickness. The thickness of the oxide layer increases as the particle size decreases. From Mössbauer study, it was found to increase thickness of oxide shell from 1.6 nm to 3.5 nm with the refinement of α-Fe core. It is in the good correspondence with the TEM observation and in the good agreement with that defined from the chemically analyzed oxygen content in nanoparticles [4].

By variation of experimental parameters such as precursor decomposition temperature, carbonyl evaporation rate and carrier gas flow rate, the mean particles size can be changed from 6 to 150 nm. Fig. 3 shows the main stages of particles’ growth. At the low temperature, particles have round shape and core-shell structure, core is metallic iron and shell is magnetite. The increasing decomposition temperature and residential time of nanoparticles in reactor increased the mean particles size and lead to more asymmetric distribution of particles size. Unagglomerated magnetic nanoparticles form intricate long threads to minimise the magnetic energy. At the higher temperature, particles coagulated and structure completely consisted of filaments of 40-100 nm in diameter depending on experimental parameters. Such structure is so unstable that new large particles are formed in the temperature of higher than 700°C and does not grow significantly as the temperature increases up to 1000°C. The mean size of these particles depends on size of initial iron particles.

![Fig. 3. SEM images for particles formation with temperature: (a) primary particles formation; (b) “chain” structure of nanoparticles; (c) new large particles formed at the high temperature.](image)

Fig. 4 shows the magnetic properties of the iron nanoparticles synthesized in various conditions. Maximal magnetization of the powder with the average particle size of 75 nm is about 210 emu/g, which is almost theoretical value of 225 emu/g known in pure bulk iron. At the smaller mean size of particles, magnetization is also in the good correspondence with values which were calculated in speculation that particles consist of iron core and magnetite shell of 2 or 3 nm thickness (\(M_s\sim 90\) emu/g). However, when the particle size is smaller than 12 nm the maximum magnetization of the particles decreases continuously. Such decrease of magnetization comes from the increase of portion of superparamagnetic particles with the decrease of mean particle size. Particles smaller them 8 nm behave like paramagnets.
In general, the coercivity of ferromagnetic materials increases with the decrease of particle size until it is maximized to the size of single magnetic domain. Then the coercivity becomes smaller and rapidly drops to a negligible value. The single magnetic domain size in a magnetic material is proportional to the factor, $A^{1/2}/M_s$. Here, $A$ and $M_s$ are the exchange energy constant and the theoretical maximal magnetization, respectively. The exchange energy of metallic pure iron is extremely small, yielding a very fine single domain size of almost 10 nm [5]. The maximum coercivity obtained so far is about 1 kOe, measured from the iron nanoparticles with the average size of 20-25 nm. It means that Fe core size is at least 15-21 nm, which is much bigger than theoretically estimated domain size.

Summary

Iron-based magnetic nanoparticles of 6-75 nm can be successfully produced by CVC method. Particle growth behavior was investigated in different conditions through microscopic examination considering formation parameters, size and structure of nanoparticles. Ultrafine particles of less than 8 nm size were superparamagnetic, maximum coercivity of iron nanoparticles obtained in this study (~ 1 kOe) was shown in the size of 20-25 nm and maximum magnetization was 210 emu/g, almost approaching the theoretical value known in pure bulk iron. Produced particles would be applicable to magnetic liquids, magnetic recording media or permanent magnets.

References


