Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 29-30, 2014

Phase analysis of iron-oxides by ^{57}Fe- Mössbauer spectroscopy

[1]*Young Rang Uhm**,*[2]*Chang Kyu Rhee,* [1]*Kwang Jae Son, and* [3]*Chul Sung Kim*

[1]*Radioisotope Research Division Korea Atomic Energy Research Institute (KAERI), Daejeon 305-353, Korea*
[2]*Nuclear Materials Research Division Korea Atomic Energy Research Institute (KAERI), Daejeon 305-353, Korea*
[3]*Department of Nano-electro Physics, Kookmin University, Seoul 136-702, Korea*
**Corresponding author: uyrang@kaeri.re.kr*

1. Introduction

Mössbauer spectroscopy using ^{57}Co for a nuclear resonance with ^{57}Fe is a powerful method for analysis of iron-containing materials [1]. This method turns out the quality of iron in target materials, which are valence state, occupied sub-site, and exchange interaction with neighbor atom, etc., [2]. Nanosize iron-metal and -oxide powders have been widely investigated for use in magnetic recording media, microwave devices, ferrofluids, biomedical application, and other industrial fields [3]. Many attempts have been made so far to develop processes and techniques for a synthesis of nanosize powders with specific functional properties. The chemical methods including precipitation techniques, sol–gel processes, and inverse-micelle methods have been used to successfully synthesize narrowly distributed nanosize powders [4]. However, since these processes are based on chemical-media, the resulting powders often undergo a surface contamination or agglomeration of the particles. On the other hand, the dry methods represented by a gas condensation process have been developed to obtain high purity nanosize powders [5], in which it is expected to suppress an agglomeration of the particles. In the present study, nanosize iron-oxide powders were synthesized by gas-phased method such as the pulsed wire evaporation (PWE) [6]. These are known as one-step synthetic technique with high efficiency and high production rate compared with other wet processes involving several treatment steps. Especially, we focus on the phase variation and characterization using Mössbauer spectroscopy of the nanopowders produced under various ambient gas conditions.

2. Experimental Technique

High purity Fe_2O_3 and Fe_3O_4 powders were synthesized by the PWE method. An argon-oxygen mixed ambient gas was supplied to the PWE chamber during the evaporation process, in which the total pressure of the mixed gas was about 1.3 bar.The crystal structure of the synthesized powders was examined by X-ray diffraction (XRD) using Cu Kradiation (λ = 1.5406 Å). The size and shape of the powders were observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Mössbauer spectra were recorded by using a conventional spectrometer of the electromechanical type with a ^{57}Co source in a rhodium matrix and then the parameters were obtained by a leastsquares fitting by assuming Lorentzian line shapes. The magnetic phase was investigated by measuring Mössbauer spectroscopy at low temperature range from 13 K to 290 K.

3. Results and discussion

In Fig. 1, the XRD patterns for the iron-oxide powders synthesized by PWE method in the mixed gas with different oxygen contents are displayed. The diffraction pattern of the powder synthesized with Ar/O_2 (30%) gas shows two phases of crystal structure, in which one is a spinel structure and the other is an additional structure corresponding to the α-Fe_2O_3 (hematite) phase, as shown in Fig. 1(a). On the other hand,the diffraction pattern of the powder synthesized with Ar/O_2 (15%) gas shows a typical spinel structure (Fig. 1(b)). However, the iron-oxide phase of the spinel structure cannot be clearly distinguished in the both XRD patterns above, because of the very similar peak positions and lattice parameters between Fe_3O_4 (magnetite) and γ-Fe_2O_3 (maghemite). Magnetite, an inverse spinel structure with a cubic unit cell, consists of two sub-structures of octahedral (O_h) and tetrahedral (T_d) sites. The octahedral site is occupied by Fe^{2+} and half of the Fe^{3+} ions, whereas the tetrahedral site is occupied by the other half of the Fe^{3+} ions. As for maghemite, however, only Fe^{3+} ions occupy both the octahedral and tetrahedral sites.

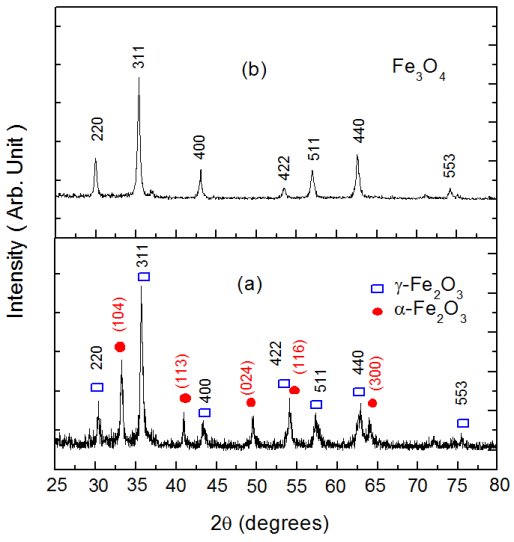

Fig. 1 X-ray diffraction patterns for the iron-oxides synthesized (a) with Ar/O_2 (30%), and (b) with Ar/O_2 (15%) gas, where the total pressure of the mixed gases was kept constant at a value of about 1.3 bar.

It means that the phase separation of the two components can be accomplished by investigating the existence of the Fe^{2+} ions. Therefore, for the phase analysis of the iron-oxide powders, we carried out Mössbauer measurement which can provide useful information on the valence state and magnetic behavior of iron ions in a crystal lattice. The spectrum was analyzed with two magnetically ordered sextets. Results of magnetic hyperfine field and isomer shift of the outer sextet is typical of the Fe^{3+} ions in α-Fe_2O_3 structure. As for the inner sextet, the values for magnetic hyperfine field and isomer shift reveal that the valence state of iron is Fe^{3+} and consequently the sextet corresponds to the α-Fe_2O_3 phase. The relative atomic fraction of the α-Fe_2O_3 and γ-Fe_2O_3 phases for the powder with Ar/O_2 (30%) were about 34 and 66%, respectively. Meanwhile, when the mixed gases with the oxygen content of below15%was introduced into the evaporation chamber, the resultant powders contained some iron metal as well as Fe_3O_4.

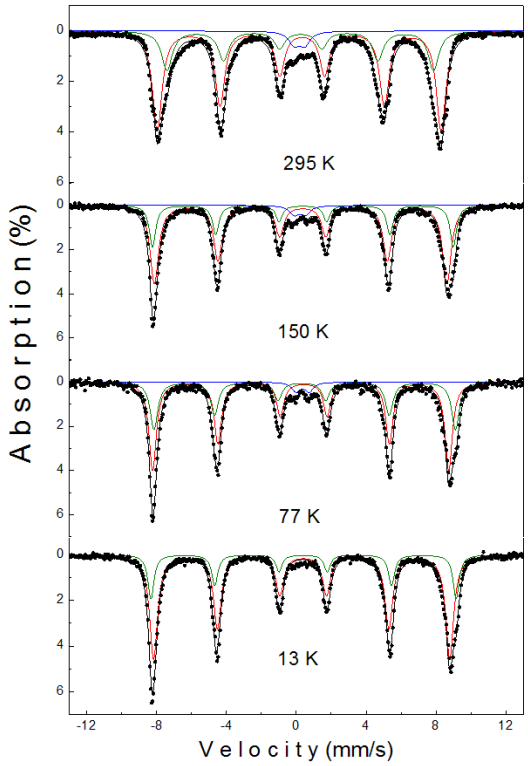

Fig 2 Mössbauer spectra for γ-Fe_2O_3 and α-Fe_2O_3 powders at various temperatures.

Mössbauer spectra for the iron-oxide powders synthesized in different oxygen concentrations showed different shapes of the absorption spectra. In the absorption spectrum of the powder synthesized with Ar/O_2 (15%) gas, one can see that the spectrum consists of two sextets, where the iron ions are magnetically ordered in the crystal lattice. Isomer shift values (δ) for the outer and inner sextets are found to be 0.18 and 0.53 mm/s relative to the iron metal, respectively, which are consistent with Fe^{3+} and Fe^{2+} charge states.We note that the Fe^{2+} state was clearly observed from the Mössbauer analysis. Also, the relative atomic fraction of the Fe^{3+} sextet and the Fe^{2+} sextet were determined to be about 65 and 35%, respectively. The Mössbauer spectrua at temperature range from 77 to 295 K consists of two sets of sextet Lorentzian lines, and a broad doublet line. Two superimposed sextet correspond to Fe^{3+} ion of α-Fe_2O_3 and γ-Fe_2O_3. A quadrupole split line in the center of the spectrum represents a superparamagnetic phase of γ-Fe_2O_3 with a mean particle size below 7 nm. The Mössbauer spectrum at 13 K consists of two sets of sextet Lorentzian lines, only. The superparamagnetic phase performed at and above 77K, as shown in Fig. 2.

4. Conclusions

Iron-oxide nanopowders were synthesized by a pulsed wire evaporation (PWE) in various ambient gas conditions. TEM measurement indicates that the spherical iron nanoparticles are about 55 nm in diameter and the thickness of the surface passivation layer is between 2 and 3 nm. As for the iron-oxide nanopowers, a mixed gas of Ar/O_2 was used as an ambient gas. The phase analysis for the produced iron-oxide powders was systemically investigated by using Mössbauer spectra and the results show that classified phases of Fe_2O_3 and Fe_3O_4 can be controlled by regulating the oxygen concentration in the mixed gas during the PWE process.

Acknowledgement

This research was supported by ‘‘Development of radioisotope production and application technology based on research reactor’’ funded by Ministry of Science, ICT & Future planning.

REFERENCES

[1] G.F. Donne, Properties of ferrites at low temperatures, Journal of Applied Physics, Vol. 81 pp. 5064, 1997.
[2] M. Allen, D. Willits, J. Mosolf, M. Young, T. Douglas, Protein Cage Constrained Synthesis of Ferrimagnetic Iron Oxide Nanoparticles, Advenced Materials, Vol. 14, pp.1562-1565, 2002.
[3] M. Chatterjee, M.K. Naskar, P.K. Chakrabarty, D. Ganguli, Sol-gel alumina fibre mats for high-temperature applications, Materials Letter, Vol. 57, pp. 87-93, 2002.
[4] S. Sun, H. Zeng, D.B. Robinson, S. Raoux, P.M. Rice, S.X. Wang, G. Li, Monodisperse MFe_2O_4(M= Fe, Co, mn), Journal American Chemical Society, Vol. 126, pp. 273–279 , 2004.
[5] H.M. Lee, Y.R. Uhm, C.K. Rhee, Phase control and characterization of Fe and Fe-oxide nanocrystals synthesized by pulsed wire evaporation method, Journal of Alloys and Compounds, Vol. 461, pp. 604–607, 2008.
[6] Y.R. Uhm, J.H. Park, W.W. Kim, C.-H. Cho, C.K. Rhee, Magnetic properties of nano-size Ni synthesized by the pulsed wire evaporation(PWE) method, Materials Science and Engineering B, Vol. 106, pp. 224–227 , 2004.