Synthesis of Ferrite Nanoparticles by Mechanochemical Processing Using a Ball Mill*1

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Ferrites with the spinel structure have a wide field of technological applications. In the present study, various ferrite (Fe₃O₄, CoFe₂O₄ and Ni_{0.5}Zn_{0.5}Fe₂O₄) nanoparticles were synthesized by mechanochemical reaction in aqueous solution of various chlorides (FeCl₃, CoCl₂ or NiCl₂/ ZnCl₂) and NaOH in a horizontal ball mill. Structures, morphologies, compositions and magnetic properties of the synthesized nanoparticles were investigated using X-ray diffraction (XRD), analytical high-resolution transmission electron microscopy (HRTEM) and vibrating sample magnetometer (VSM). It was revealed that the particle size of the ferrite nanoparticles can be controlled by milling conditions, such as the milling time and the pH value (*R* value) of starting solution. The average size of Fe₃O₄ particles milled for 259.2 ks and 432.0 ks at *R* = 1 were 30 nm and 20 nm, respectively. Also, the particles milled for 259.2 ks at *R* = 0.5 had the size of 100 nm. The formation of Fe₃O₄ nanoparticles from the aqueous solutions with the different *R* values proceeded *via* two different processes. In the case of *R* = 1, *α*-Fe nanoparticles formed first, and then oxidized to become Fe₃O₄ nanoparticles. Meanwhile, in the case of $R \neq 1$, α -FeOOH phase formed, and changed to Fe₃O₄ nanoparticles by milling. For magnetic properties, the magnetization at 1.2 MA/m was the value of 72 µWb·m/kg after milling for longer than 86.4 ks with *R* = 1. The coercivity was the maximum of 10.8 kA/m after milling for 259.2 ks with *R* = 0.5. The particle sizes of CoFe₂O₄ milled for 259.2 ks at *R* = 1 and Ni_{0.5}Zn_{0.5}Fe₂O₄ milled for 345.6 ks at *R* = 1 were about 30 nm. The magnetization values of CoFe₂O₄ and Ni_{0.5}Zn_{0.5}Fe₂O₄ were about 55 µWb·m/kg, with coercivity values of 43.4 kA/m and 5.3 kA/m, respectively.

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1. Introduction

Recently, electronic devices, such as a personal computer and a cellular phone, have been spread by development of information technology. Because of this, there has been an increasing demand for development of various electromagnetic materials, e.g., high-density magnetic recording media and electromagnetic wave absorption materials. The spinel ferrites have been attracting attention since they exhibit wide variety of electromagnetic properties depending on the structure and composition. The spinel ferrites, known as the ferrimagnetic oxide, have the general form of MeFe₂O₄, where *Me* is a divalent metallic ion, such as Fe^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} . These divalent metallic ions can be distributed on the tetrahedral position (A-site) surrounded by four oxygen ions, or the octahedral position (B-site) surrounded by six oxygen ions in the spinel structure. The composition and distribution of Me ions significantly affect the electronic and magnetic properties. Generally, various ferrites particles are prepared from aqueous solutions by precipitation method. Kiyama et al.¹⁻⁴⁾ and Ishikawa et al.⁵⁾ have reported the optimum condition for the formation of ferrite particles from the aqueous solutions of ferrous salts, in which alkaline solutions were added as precipitation agents. According to their reports, the formation of ferrite particles sensitively depends on temperature, pH value in solutions and so on. In the present study, ferrite nanoparticles were synthesized by controlling the milling conditions, *i.e.* the milling time and the pH value in the starting solution, in mechanochemical processing using a ball mill. Mechanochemical processing makes use of enhancement of chemical reactions by mechanical energy. Chemical reactions, which normally require high temperatures, can be thus activated during milling. In the auxiliary experiment, the solution (R = 1)consisting of FeCl₃ and NaOH was left for a few weeks or stirred for a few hours at room temperature. The synthesized particles were dark reddish-brown, and the X-ray diffraction pattern from the particles were amorphous-like. Although the particles cannot be identified, the synthesized particles were not Fe₃O₄. It seems that Fe₃O₄ particles cannot be synthesized by only leaving or stirring the solution with R = 1 at room temperature. In the mechanochemical processing using a ball mill, however, the Fe₃O₄ particles were synthesized from the solution because of the chemical reactions activated by mechanical energy in the ball milling. Ding et al.^{6–9)} have, previously, synthesized a number of metallic, oxide and sulfide nanoparticles by the mechanochemical processing using a ball mill. Suitably designed displacement reactions in solid state have been shown to generate uniform nanoparticles in a soluble by-product phase. Selective removal of the by-products phase results in the separated nanoparticles of the desired phase.

In the present study, the nanoparticles of various spinel ferrites, Fe_3O_4 , $CoFe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$, were synthesized by mechanochemical processing, using the reaction in the solution consisting of various chlorides (FeCl₃, CoCl₂ or NiCl₂/ZnCl₂) and NaOH. In the spinel ferrites, Fe_3O_4 is the most fundamental system. $CoFe_2O_4$ has high magnetocrystalline anisotropy, and also $Ni_{0.5}Zn_{0.5}Fe_2O_4$ can be used as electromagnetic wave absorbers for high frequency. The structures, morphologies and magnetic properties for the synthesized nanoparticles were investigated.

2. Experimental Procedure

2.1 Synthesis of ferrite nanoparticles

The nanoparticles of the various ferrites, Fe₃O₄, CoFe₂O₄

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and Ni_{0.5}Zn_{0.5}Fe₂O₄, were synthesized by mechanochemical reaction. The aqueous solutions (100 g) consisting of various chlorides (FeCl₃, CoCl₂ or NiCl₂/ZnCl₂) and NaOH were milled using a horizontal ball mill $(180 \pm 1 \text{ min}^{-1})$ using SUS304 balls (ϕ 9.6 mm, 1 kg) and SUS304 vial (500 cm³). The Fe₃O₄ nanoparticles were synthesized by milling for various times in the starting solution with R = 1, where R is defined as the molar ratio of OH⁻ and Fe³⁺ in the starting solution, *i.e.* $R = 3[OH^{-}]/[Fe^{3+}]$. Also, the R value (pH value) in the starting solution was changed by adding various amounts of NaOH, and the nanoparticles were synthesized by milling in the starting solutions with various R values. In the synthesis of CoFe₂O₄ and Ni_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles, the *R* value is defined as $R = 4[OH^-]/[Fe^{3+}]$, and their nanoparticles were synthesized for various times in the starting solution with R = 1. The solution and the balls were loaded and sealed under air. The vial temperature was kept constant during the experiments by air cooling. The pH values of the colloidal solutions after milling were measured using a pH meter. The colloidal solution was diluted with deionized water, and then the synthesized nanoparticles were separated from the colloidal solution using a centrifuge. After removing the solution, the nanoparticles were dried by evacuating at room temperature.

2.2 Characterization of ferrite nanoparticles

X-ray diffraction (XRD) measurements were carried out on a Rigaku RINT-2200 diffractometer with Co-K_{α} radiation $(\lambda = 0.1789 \text{ nm})$ generated at 30 kV and 30 mA. The nanoparticles were mounted on a glass sample holder in the glove box filled with Ar (<0.1 ppm O₂) and the surface was covered by a collodion/isoamyl acetate solution to prevent oxidation before exposing the sample to air. The nanoparticles were observed on a HITACHI H-800 transmission electron microscope (TEM) operated at 200 kV. Highresolution transmission electron microscopy (HRTEM) and composition analysis were carried out on a JEOL JEM-2010 equipped with a Voyager III energy dispersive X-ray spectroscopy (EDX) system operated at 200 kV. For the TEM samples, the nanoparticles were dispersed ultrasonically in isopropyl alcohol and put onto a carbon coated copper grid. The H₂ gas produced during a ball milling was analyzed on a SHIMAZU GC-4BPT gas chromatograph using a carrier gas of Ar. The sample gas of 20 mm³ was collected from the milling vial, and then was fed into the gas chromatograph. The magnetic measurements of the nanoparticles were carried out on a Riken Denshi BHV-55 vibrating sample magnetometer (VSM) at room temperature. The saturation magnetization was measured at a maximum field of 1.2 MA/m. The nanoparticles was loaded in a polymer vial, then was sealed and fixed by grease.

3. Results and Discussion

3.1 Fe₃O₄ nanoparticles

3.1.1 Synthesis of Fe₃O₄ nanoparticles

Figure 1 shows the pH values of the colloidal solutions after milling for various time with R = 1. The pH values increased rapidly with milling time for the first 86.4 ks, and started to level off at the value of about 10.5 at milling time



Fig. 1 pH values of colloidal solutions after milling for various time with R = 1.



Fig. 2 XRD patterns of nanoparticles after milling for various time with R = 1. Values (hkl) are marked for the spinel structure.

longer than 86.4 ks. It is suggested that the chemical reactions in the starting solution finished completely with the first 86.4 ks milling.

The XRD patterns of the synthesized nanoparticles after milling for various time with R = 1 are shown in Fig. 2. The peak positions agree with those of the spinel structure. Thus the synthesized nanoparticles are Fe₃O₄ and/or γ -Fe₂O₃



Fig. 3 TEM images of Fe_3O_4 nanoparticles after milling for various time with R = 1.

phases. Although the patterns of Fe₃O₄ and γ -Fe₂O₃ phases are similar,^{10,11)} some peaks corresponding to γ -Fe₂O₃ phase, such as (110), (210) and (211) peaks, can not be seen in the XRD patterns. Therefore, the synthesized nanoparticles seem to be Fe₃O₄ phase. In these diffraction patterns, no trace of the reactants and by-products, *i.e.* FeCl₃, NaOH, NaCl and so on, can be seen. The diffraction peaks after milling for 21.6 ks are broad, that is, the nanoparticles milled for short time seem to be amorphous-like. Those peaks become sharper with milling time, indicating that the nanoparticles are crystallized by mechanical energy during milling process. In the nanoparticles milled for short time, it can be seen the peak from α -Fe phase at around 52.4 deg. The peak disappeared with further milling.

Figure 3 shows the TEM images of the Fe_3O_4 nanoparticles after milling for various time with R = 1. In the TEM image of the sample after milling for 21.6 ks, the aggregated particle consisting of numerous particles of a few nanometers can be seen. The particle sizes after milling for 43.2 ks and 86.4 ks had a wide distribution between a few nm and 100 nm. The images of the nanoparticles milled for more than 86.4 ks show that the particle size decreases with milling time and becomes more uniform. In the nanoparticles milled for 259.2 ks, the size was between a few nm and 50 nm, and also the nanoparticles milled for 432.0 ks and 864.0 ks were about 20 nm in diameter. The crystallite size estimated with the width of the spinel (311) peak in Fig. 2 using the Scherrer equation.¹²⁾ In the nanoparticles after milling for 259.2 ks, 432.0 ks and 864.0 ks, their crystallite sizes were 18 nm, 14 nm and 12 nm, respectively. Those crystallite sizes estimated using the Scherrer equation agree well with the particle sizes measured from the TEM images (Fig. 3). The above results indicate the following: the chemical reactions in the starting solution with R = 1 finish completely within the first 86.4 ks milling. The Fe_3O_4 nanoparticles form and grow in the period. Then, the synthesized nanoparticles are grinded by milling. In the ball milling, the grinding is one of the important effect in order to form the nanoparticles with uniform particle size, as well as the activation effect of chemical reaction. Size of the nanoparticles reach the final diameter of about 20 nm and become uniform after milling for more than 432.0 ks.

Figure 4 shows the XRD patterns of the synthesized nanoparticles after milling with various *R* values for 259.2 ks. It can be seen that the peak positions agree with those of the spinel structure, *i.e.* Fe₃O₄ phase, in all the patterns. In the patterns of the nanoparticles milled with $R \neq 1$, other peaks are also seen. Those peak positions coincide with those for the α -FeOOH (goethite) phase.¹³⁾

The TEM images of the synthesized nanoparticles after milling with various R values for 259.2 ks are shown in Fig. 5. The two different morphology, needle and irregular



Fig. 4 XRD patterns of nanoparticles after milling with various *R* values for 259.2 ks.



R = 0.67



Fig. 5 TEM images of nanoparticles after milling with various *R* values for 259.2 ks.

shapes, can be seen in the images of the nanoparticles milled with $R \neq 1$. From the XRD measurements (Fig. 4), the needle shaped nanoparticles are the α -FeOOH phase, and others are Fe₃O₄ phase. The particle size of the Fe₃O₄ phase increased with the smaller *R* values between 0.5 and 2.0. It was possible to separate the Fe₃O₄ from α -FeOOH nanoparticles by an application of magnetic field because α -FeOOH phase is antiferromagnetic.

3.1.2 Formation process of Fe₃O₄ nanoparticles

It is considered that mechanical energy accompanying collisions between balls and ball/vial during milling is necessary to synthesize Fe₃O₄ nanoparticles. To confirm this, similar experiments were conducted without balls with the aqueous solution with R = 1. The XRD results indicated that Fe₃O₄ nanoparticles do not form even after prolonged milling for 432.0 ks. Therefore, it is apparent that the mechanical energy supplied by ball milling is necessary for the formation of Fe₃O₄ nanoparticles.

The XRD patterns in Fig. 2 show that the nanoparticles milled for less than 86.4 ks with R = 1 consisted of α -Fe and Fe₃O₄ phases. This suggests that α -Fe nanoparticles first form from the aqueous solution of FeCl3 and NaOH with R = 1 during the milling, then they are oxidized to Fe₃O₄. For the oxidization of α -Fe nanoparticles, oxygen can be supplied from the air in the milling vial. Also, it is possible that oxygen is generated by the decomposition of H₂O in the aqueous solution. Oxidation of α -Fe particles with the H₂O decomposition is possible since the free energy change, ΔG , of Fe₃O₄ from α -Fe and O₂ at 293 K is -1017.0 kJ/mol and the ΔG of the H₂O decomposition to H₂ and O₂ is 238.0 kJ/ mol.¹⁴⁾ To investigate if the oxidation of α -Fe nanoparticles is due to the H₂O decomposition, the milling of the aqueous solution with R = 1 for 259.2 ks was carried out in the vial atmosphere of Ar. The water for the aqueous solution was deoxygenated. The synthesized nanoparticles were the spinel structure in the XRD pattern. Also, the gas in the vial after milling for 432.0 ks, which was carried out in the vial atmosphere of air, was analyzed using a gas chromatography, and the existence of H₂ gas (about 90 vol%) was confirmed. These results indicate that the oxidation of α -Fe nanoparticles by the oxygen generated by decomposition is primary formation mechanism for Fe₃O₄ nanoparticles.

Meanwhile, the XRD patterns in Fig. 4 show that the α -FeOOH phase synthesized after milling with $R \neq 1$. Figure 6 shows the XRD patterns of the nanoparticles synthesized after milling for various time with R = 0.5. Although the peaks corresponding to α -FeOOH phase can be seen after milling for 86.4 ks, the intensity of those peaks decreased with milling time. On the other hand, the peaks of the spinel phase appeared after milling for 172.8 ks, and the intensity of those peaks increased with milling time. This result indicates that the α -FeOOH phase is synthesized first from the aqueous solutions with $R \neq 1$, then is oxidized to become the Fe₃O₄ nanoparticles by mechanical energy during milling.

3.1.3 Magnetic properties of Fe₃O₄ nanoparticles

Figure 7 shows the magnetic curves for the Fe₃O₄ nanoparticles milled for 21.6 ks and 86.4 ks with R = 1. Similar curves were observed for the nanoparticles milled for 86.4 ks or longer. The both magnetization curves were not saturated at 1.2 MA/m. It seems that part of the synthesized nanoparticles are superparamagnetic because their particle sizes are smaller than the critical size for single domain particle for Fe₃O₄ (about 40 nm⁴), supported by the TEM observations in Fig. 3. The magnetization and coercivity of the Fe₃O₄ nanoparticles milled for various time with R = 1 are shown in Fig. 8. The magnetization at 1.2 MA/m



Fig. 6 XRD patterns of nanoparticles after milling for various time with R = 0.5.



Fig. 7 Magnetization curves of Fe_3O_4 nanoparticles after milling for 21.6 ks and 86.4 ks with R = 1.

increased rapidly with milling time because of the crystallization of the nanoparticles, corresponding to the results of the XRD measurements in Fig. 2. The magnetization started to level off at the value of about 72 μ Wb·m/kg. This value, however, is lower than the reported magnetization of Fe₃O₄ phase at room temperature (116 μ Wb·m/kg¹⁵). It is because the synthesized nanoparticles are superparamagnetic, and also their structures are imperfect with the vacancies in the octahedral positions. In the XRD patterns shown in Fig. 2, the intensity of the (222) reflection was extremely weak, indicating that the octahedral positions have some vacancies.¹⁶) The coercivity of the nanoparticles after milling between 86.4 ks and 172.8 ks was about 6.8 kA/m, and decreased with milling time. It is well known that coercivity is sensitive to magnetic domain size, which limited by the



Fig. 8 Magnetization at 1.2 MA/m and coercivity of Fe_3O_4 nanoparticles after milling for various time with R = 1.



Fig. 9 Influence of crystallite size on coercivity of Fe₃O₄ nanoparticles.

particle size. In the present study, the particle sizes measured from the TEM images are close to the crystallite sizes estimated from the XRD patterns. Therefore, it is considered that the coercivity of the synthesized nanoparticles depends on the crystallite size. Figure 9 shows the influence of crystallite size on the coercivity of the synthesized nanoparticles. Thus, the coercivity and the crystallite size exhibit a good correlation. It also indicates that the particle sizes of the synthesized nanoparticles are smaller than the single magnetic domain size of Fe_3O_4 and the nanoparticles are superparamagnetic because the coercivity increased with the crystallite size.

3.2 CoFe₂O₄ nanoparticles

Figure 10 shows the TEM image of the nanoparticles synthesized after milling for 259.2 ks. It can be seen that the nanoparticles are about 30 nm in diameter. The result of XRD measurement indicated that the crystal structure of nanoparticles is the spinel structure. The compositions of the individual nanoparticles, determined by an analytical HRTEM, were 21.7 at%Co and 78.3 at%Fe, indicating a deficiency of approximately 15 at%Co from the stoichiometric composition of CoFe₂O₄.

Figure 11 shows the magnetic curve of the CoFe₂O₄ nanoparticles milled for 259.2 ks. The magnetization and coercivity were 56.5 μ Wb·m/kg and 43.4 kA/m, respectively. This magnetization value is lower than the value of CoFe₂O₄ at room temperature (101 μ Wb·m/kg¹⁵). It seems that part of the synthesized nanoparticles are superparamagnetic because



Fig. 10 TEM images of $CoFe_2O_4$ nanoparticles milled for 259.2 ks with R = 1.



Fig. 11 Magnetization curves of $CoFe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ synthesized nanoparticles.

their particle sizes are smaller than the critical size for single domain particle for CoFe₂O₄, which is approximately 60 nm,¹⁷⁾ supported by the TEM observations in Fig. 10. In the XRD pattern, the intensity of the (222) reflection was extremely weak, indicating that the octahedral positions have some vacancies. The above result is also supported by the composition analysis of the individual nanoparticles. According to the composition analysis, the deficiency of the Co concentration from the stoichiometric composition of CoFe₂O₄ was exhibited. If the deficiency of the Co concentration is the vacancies in the octahedral positions, the octahedral positions are occupied by the Co^{2+} of 18.5 at% and the vacancies of 14.8 at%. On the basis of this assumption the calculated magnetization is 56 µWb·m/kg. Since the calculated value is closed to the magnetization of the synthesized CoFe₂O₄ nanoparticles in the present study, it is indicated that the octahedral positions consist of Co²⁺ and some vacancies. Therefore, the magnetization of the synthesized CoFe₂O₄ nanoparticles is lower than the reference value.

3.3 Ni_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles

Figure 12 shows the TEM image of the nanoparticles synthesized after milling for 345.6 ks. It can be seen that the nanoparticles are about 30 nm in diameter. The result of XRD measurements indicated that the crystal structure of nanoparticles was the spinel structure. The compositions of the individual nanoparticles, determined by an analytical HRTEM, were 7.4 at%Ni, 13.6 at%Zn and 79.0 at%Fe, indicating a deficiency of approximately 10 at%Ni from the stoichiometric composition of Ni_{0.5}Zn_{0.5}Fe₂O₄.

Figure 11 shows the magnetization curve of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles milled for 345.6 ks. The magnetization and coercivity were 54.0 μ Wb·m/kg and 5.3 kA/m, respectively. This magnetization value is lower than the value of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at room temperature (148 μ Wb·m/kg¹⁵). This is because part of the synthesized nanoparticles are superparamagnetic, and their crystal structures are imperfect with the vacancies, similarly to the case of



Fig. 12 TEM images of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles milled for 345.6 ks with R = 1.

CoFe₂O₄ nanoparticles. If the octahedral positions have some vacancies, the magnetization of Ni_{0.5}Zn_{0.5}Fe₂O₄ decreases. In the XRD pattern shown, the intensity of the (222) reflection is weak, indicating that the octahedral positions have some vacancies. The above result is also supported by the composition analysis of the individual nanoparticles. The deficiency in Ni concentration from the stoichiometric compositions have some vacancies. Therefore, the magnetization of the synthesized Ni_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles is lower than the reference value.

4. Conclusion

The nanoparticles of the various spinel ferrites (Fe₃O₄, CoFe₂O₄ and Ni_{0.5}Zn_{0.5}Fe₂O₄) were synthesized from the aqueous solutions consisting of various chlorides (FeCl₃, CoCl₂ or NiCl₂/ZnCl₂) and NaOH by mechanochemical processing using a ball mill. The structures, morphologies and magnetic properties in their synthesized nanoparticles were studied and can be summarized as follows:

- (1) The formation of Fe₃O₄ nanoparticles from the aqueous solutions with the different *R* values proceeded *via* two different processes. In the case of R = 1, α -Fe nanoparticles were firstly synthesized, and then were oxidized to Fe₃O₄ nanoparticles. In the case of $R \neq 1$, α -FeOOH phase formed, and changed to the Fe₃O₄ nanoparticles by milling.
- (2) The Fe₃O₄ nanoparticles with different particle sizes could be synthesized by changing the milling time and the *R* value in the starting solution. The particle size was controllable between 20 and 100 nm. In magnetic properties, the magnetization was the value of $72 \,\mu\text{Wb}\cdot\text{m/kg}$ after milling for longer than 86.4 ks with R = 1. The coercivity showed the maximum of 10.8 kA/m after milling for 259.2 ks with R = 0.5.
- (3) The CoFe₂O₄ nanoparticles were synthesized by milling for 259.2 ks nanoparticles, were about 30 nm in diameter. The magnetization and coercivity were 56.5 μWb·m/ kg and 43.4 kA/m, respectively.
- (4) The Ni_{0.5}Zn_{0.5}Fe₂O₄ nanoparticles were synthesized by milling for 345.6 ks nanoparticles, were about 30 nm in diameter. The magnetization and coercivity were $54.0 \,\mu$ Wb·m/kg and $5.3 \,$ kA/m, respectively.
- (5) In the synthesized nanoparticles of Fe₃O₄, CoFe₂O₄ and Ni_{0.5}Zn_{0.5}Fe₂O₄, their magnetization values were lower than the reference values because part of the synthesized nanoparticles are superparamagnetic and their crystal structures are imperfect with the deficiency of cations in *B*-sites. It seems that the deficiency of cations can be improved by changing the composition in the starting solution.

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