Mössbauer spectroscopy study of the high energy ball milling (HEBM) synthesis & kinetics of CoFe$_2$O$_4$ from Co(OH)$_2$ and $\alpha$-Fe$_2$O$_3$

Oswald N C Uwakwe, Richard Pérez Moyet

Department of Engineering Science and Materials, University of Puerto Rico-Mayagüez, P. O. Box 9044, Mayagüez, Puerto Rico 00681-9044
uwakweh@ece.uprm.edu

Abstract.

Room temperature mechanochemical synthesis of single phase nanosized particles of CoFe$_2$O$_4$ by HEBM of stoichiometric mixtures of Co(OH)$_2$ and $\alpha$-Fe$_2$O$_3$ under wet acetone was achieved after 25 hours of continuous ball milling. The particle size and lattice constant were 98.13 nm, and 8.398 Å after 10 hours, while 31.96 nm and 8.343 Å after 25 hours. The coercivity (25 hours state) was 12.78 mT with saturation and remanent magnetizations of 27.52 Am$^2$/kg and 3.94 Am$^2$/kg respectively due to small amount of a magnetic phase. Mössbauer spectroscopy measurements showed very limited reaction in 5 hours, with the single phase forming directly to superparamagnetic particles. The quadrupole splitting of the doublets was in the range of 0.24-1.14 mm/s, with corresponding isomer shift range of 0.80 -0.67 mm/s. The DSC measurements of the single phase material showed that it was metastable with characteristic stages whose activation energies were determined by the modified Kissinger kinetic analyses to be in the range of 3.51 kJ/mol to 11.89 kJ/mol.

1. Introduction

The oxides called spinel ferrites or ferrospinels are designated as MFe$_2$O$_4$ with “M” as the divalent cation different from the Fe trivalent cation based on their location within the crystal lattice. Néel [1], suggested that small antiferromagnetic particles can exhibit superparamagnetism and weak ferromagnetism due to uncompensated spins in the two sublattices. They are used in a host of scientific and technological applications such as in magnetic and switching devices [2-4] where their performance can be related to their compositions, microstructure, cationic distributions, and synthesis/processing histories [5].

CoFe$_2$O$_4$ is a well known hard magnetic material with very high cubic magnetocrystalline anisotropy, relatively high coercivity combined with moderate saturation magnetization. This explains why the material has a high potential for magnetic storage applications [6], with varied synthesis techniques such the modified coprecipitation method [7] etc. The synthesis based on high energy ball milling or mechanical alloying [8, 9] is among those used to obtain structures and properties that would have been otherwise impossible. Further, the mechanochemical synthesis route in obtaining a host of ferrite materials [10-11] is known to be valid alternatives to the conventional ceramic synthesis. Based on these, we undertook mechanochemical synthesis starting from solid precursors of
Co(OH)$_2$ and α-Fe$_2$O$_3$ to investigate both its formation into the single phase, subsequent evolution with HEBM, and its thermal stability behaviour [12, 13].

2. Experimental

The solid precursors used for this study were Alfar Aesar supplied Co(OH)$_2$ and α-Fe$_2$O$_3$, weighed out in stoichiometric amounts to yield the single phase cobalt ferrite via the reaction scheme: Co(OH)$_2$ + α-Fe$_2$O$_3$ → CoFe$_2$O$_4$ + H$_2$O, by ball milling 8 g of powder in a Fritsch Pulverisette-4 mill. The setting was 1400 rpm for the main disc, with a R-ratio – 3.0. 17 tempered steel grinding balls (10 mm diameter), a ball-to-powder ratio (BPR) of 40:1, and addition of 0.6 ml of acetone to the initial material mixture was used. The grinding jar was WC lined. Milling operations were stopped intermittently to retrieve powder samples for analyses.

The X-ray diffraction (XRD) was performed with a Siemens D500 diffractometer with CuK$_\alpha$ radiation. Debye Scherrer formula was used to determine the lattice parameters, while Williamson-Hall [14] analysis was used to determine the particle size and strain values. The magnetic properties were determined with a Lakeshore 7400 Series VSM. Mössbauer spectroscopic measurements were done with a WEBRES spectrometer (SEECO Company) operating at constant acceleration mode with a 50 mCi $^{57}$Co gamma ray source in Rh matrix, and calibrated with α-Fe metal. Data was analyzed with WMOSS available at www.SEECo.us.

The thermal stability study was done with a differential scanning calorimeter (TA instrument (DSC-Q20) operated in nitrogen atmosphere (99.99 %) at 50 mL/min flow rate. Temperature and heat flow calibrations was done with a 10.5 mg indium, while the base calibration was carried out with an Al crucible.

3. Result and discussion

3.1 X-ray diffraction (XRD) measurements

Figure 1 shows XRD spectra of the manual mixture of Co(OH)$_2$, and α-Fe$_2$O$_3$ and its evolution with ball milling. As shown, new peaks emerged, with the disappearance of some corresponding to the precursor materials. The spectra showed both shifts in peaks positions, with their broadening as well. The progressive formation of the single phase CoFe$_2$O$_4$ commenced after 5 hours of ball milling, while structural changes including increase in structural defects resulted with ball milling time.

![Figure 1: XRD spectra of the mechanochemical synthesis of CoFe$_2$O$_4$ as a function of time](image-url)
The lattice constant, average internal strain, and particle size for the 10 hours milled state were, 8.398 Å, 0.00419 mm/mm, and 98.13 nm, respectively, in contrast to the corresponding values for the 25 hours milled state which were, 8.343 Å, 0.00004 mm/mm, and 31.96 nm.

3.2 Vibrating Sample Magnetometer (VSM) and Mössbauer spectroscopy (MS) measurements

The magnetization of spinel ferrites originates from the difference in the magnetic moments of the cations distributed in the tetrahedral and octahedral interstitial sites, and as a consequence directly points to the distribution of the magnetic Fe$^{3+}$ and Co$^{2+}$ ions in the two sublattices. Since ball milling caused a disruption of the crystallinity of the lattice, therefore the magnetization behaviors would change during mechanochemical synthesis, as shown in Figure 2. Based on XRD measurements, complete synthesis occurred after 25 hours of ball milling, therefore the coercivity, saturation and remanent magnetization values corresponding to the VSM hysteresis plot were due to the single phase nanosized CoFe$_2$O$_4$ material. The coercivity was 12.78 mT, with the corresponding saturation and remanent magnetization 27.52 Am$^2$/kg and 3.94 Am$^2$/kg respectively.

![Figure 2: VSM measurements of the synthesis of CoFe$_2$O$_4$ by HEBM](image)

![Figure 3: Mössbauer spectra of CoFe$_2$O$_4$ by mechanochemical synthesis from Co(OH)$_2$ and α-Fe$_2$O$_3$](image)

The Mössbauer spectra of Figure 3 showed the progressive increase in intensity of the central portion with milling. The spectrum for the 25 hours milled material was fitted with a sextet, two doublets, and a singlet using the model by Rancourt and Ping [15]. It should be noted that the hyperfine distribution model of WMOSS (the program used in the spectral analyses) is an implementation of the Voigt based fitting method. In this model, each Fe site does not represent a single homogeneous iron species, but an ensemble of iron atoms with a Gaussian distribution in their internal field. Their relative abundances were 6.3%, 35.7%, 21.9%, and 36.1% correspondingly. The
quadrupole splitting and isomer shifts of the doublets were: 0.24 mm/s and 0.81 mm/s; and 1.14 mm/s and 0.67 mm/s respectively. The degree of inversion $\lambda$ referring to the sites occupancy based on the designation $(M^{2+}, Fe^{3+})(M^{2+}, Fe^{3+})_2 O_4$, where, $M$ = Co, Mg, etc., varies as a function of processing history, and was not determined at the temperature of measurement.

The singlet isomer shift was 0.52 mm/s. The internal magnetic field of sextet was 311 kOe, and accounted for the weak coercivity recorded in the VSM measurements. Possible particle size distribution with varying cationic arrangements may have contributed to doublets and singlet observed associated with Fe$^{3+}$ and Fe$^{2+}$ in the octahedral and tetrahedral sites. With the corroborating XRD results, the paramagnetic peaks were associated with superparamagnetism due to the nanosized particles of the mechanosynthesized phase, as the particle agglomeration leading to magnetic ordering did not occur based on prior SEM observation.

3.3 Thermal stability via differential scanning calorimetry (DSC) measurements

The thermal evolution of the single phase metastable CoFe$_2$O$_4$ corresponding to the 25 hours of ball milled state are shown in Figure 4, with the analyzed five characteristic stages shown on the 35ºC/min trace only. The corresponding values for the other traces were used in the modified Kissinger method for non-isothermal kinetic analyses (similar to Lui and Uwakwe [12, 13]) to obtain the activation energies corresponding to the physical phenomena associated with them. These activation energies were obtained by plotting the following expression: $\ln(T_f^2/\phi) = (E/R)1/T_f + \ln(E/Rk_0)$, where $T_f$ = characteristic temperature, $\phi$ = heating rate, E, R, and $k_0$ are activation energy, gas constant, and kinetic parameter respectively. Since it is known that HEBM process in general induces physical phenomena such as inter/intra-particles pores on ceramic materials among other structural defects, therefore, the characteristic stages identified on the DSC traces could be associated with the elimination of, and/or rearrangements of surface atoms.

![Figure 4: DSC traces of the mechanochemical synthesized CoFe$_2$O$_4$ from Co(OH)$_2$ and $\alpha$-Fe$_2$O$_3$ solid precursors](image)

The activation energies were 3.51 kJ/mol, 3.38 kJ/mol, 3.72 kJ/mol, 5.41 kJ/mol and 11.89 kJ/mol respectively, and are compatible with non-energetically tasking processes since the DSC measurements were done over temperature ranges where volume atomic diffusion in the material would be low. Further, it was not possible to associate the activation energies determined to the elimination or rearrangements of structural defects such as the zero order types (e.g., vacancies, or
interstitials types, etc.) because of their relatively small values, and also, because they were observed at low temperatures were they should be substantially immobile. This showed that tailor-made materials could be realized after HEBM based on these measurements.

4. Conclusions

1. The mechanochemical synthesis of single phase CoFe$_2$O$_4$ by HEBM of stoichiometric amounts of Co(OH)$_2$ and α-Fe$_2$O$_3$ whose physical properties depended on milling time was demonstrated. The average particle size of 31.96 nm, and corresponding lattice constant of 8.343 Å determined for the 25 hours milled material.

2. The Mössbauer measurements showed non-magnetic Fe sites corresponding to two doublets and a singlet at room temperature that were associated with superparamagnetism arising from the nanosized particles. The origin of the two doublets and singlet Fe sites could be due to particle size distribution and presence of other effects such as structural defects associated with HEBM. The Fe site associated with the magnetically split portion of the spectrum with an internal field of 311 kOe accounted for the hysteresis observed in the VSM measurements. The corresponding coercivity in the 25 hours milled material was 12.78 mT, with saturation magnetization of 27.52 Am$^2$/kg, and remanent magnetization of 3.94 Am$^2$/kg.

3. The DSC measurements showed kinetically related stages with activation energies of 3.5 kJ/mol, 3.38 kJ/mol, 3.72 kJ/mol, 5.41 kJ/mol, and 11.89 kJ/mol. All the results point to the metastable state of the HEBM material.

The support of NSF-DMR PREM at UPRM on grant No. 0351449 is hereby acknowledged.

References

[1] Néel A L 1961 Compt. Rend. 252 4075
[2] Chantrell R W and O’Grady K 1994 Appl. Magnetism (Kluwer Academic, The Netherlands 113
[3] Nakamura T, Tsutaoka T and Hatakeyama H 1994 J. Magn. Magn. Mater 138 319
[4] Tsutaoka T, Ueshima Y, Tokunaga T, Nakamura T and Hatakeyama K 1995 J. Appl. Phys. 78 3983
[5] Clark T M and Evans B J 1997 IEEE Trans. Magn. 33 3745
[6] Goldman A 1990 A Modern ferrite Technology (New York, Van Nostrand Reinhold)
[7] Cedeño-Mattei Y, Perales-Pérez O, Osorio-Cantillo C and Uwakweh O N C 2009 NSTI-Nanotech-2009 ISBN 978-1-4398-1782-7 1 109-12
[8] Ding J, Miao W M, McCormick P G and Street R 1995 Solid State Commun 95 31
[9] Ding J, Miao W M, McCormick P G and Street R 1997 J. Magn. Magn. Mater. 171 309
[10] Druska P, Steinike U and Šepelák V 1999 J. solid State Chem. 146 13
[11] Šepelák V, Baabe D, Mienert D, Litterst F J and Becker K D 2003 Script. Mater. 48 961
[12] Liu Z T and Uwakweh O N C 1996 J. Mater. Research 11 1665-72
[13] Zhentong Lui and Oswald N C Uwakweh 1997 Metallurgical and Materials Trans A 28, 743
[14] Williamson G K and Hall W H 1953 Acta Metall. 1 22
[15] Rancourt D G and Ping J Y 1991 Nucl. Instr. Meth B58 85-97