

Magnetic nanoparticles produced by surfactant-assisted ball milling

V. M. Chakka, B. Altuncevahir, Z. Q. Jin, Y. Li, and J. P. Liu^{a)}

Department of Physics, The University of Texas at Arlington, Arlington, Texas 76019

(Presented on 1 November 2005; published online 24 April 2006)

Nanoparticles of Fe, Co, FeCo, SmCo, and NdFeB systems with sizes smaller than 30 nm and narrow size distribution have been successfully prepared by ball milling in the presence of surfactants and organic carrier liquid. It has been observed that the nanoparticles prepared by milling Fe and FeCo powders were close to spherical in their shapes, whereas those of Co, SmCo, and Nd-Fe-B showed elongated rod shapes. The nanoparticles showed superparamagnetic behavior at room temperature, except for the SmCo nanoparticles that were ferromagnetic. Nanoparticles of all types showed ferromagnetic behavior at low temperatures. The compositions of nanoparticles prepared by milling the SmCo, NdFeB, and FeCo powders were found to be deviated from the starting powders. © 2006 American Institute of Physics. [DOI: 10.1063/1.2170593]

I. INTRODUCTION

One of the approaches for preparation of magnetic nanoparticles is by surfactant-assisted ball milling, a technique used for making magnetic fluids.¹⁻³ Surfactants aid in achieving smaller particle sizes during milling and dispersing the fine particles when appropriate solvents are used.⁴⁻⁶ However, the size distribution of the particles obtained by ball milling can be quite wide compared with the chemical methods. The chemical methods, nevertheless, have had limited success in the synthesis of hard magnetic nanoparticles of rare-earth compounds.^{7,8} Traditionally, surfactant-assisted ball milling technique has been used mainly for preparing ferrite nanoparticles, and not many studies have been conducted on the preparation of nanoparticles of different materials, except a few.^{9,10} In this study, systematic efforts have been made to prepare and study the properties of the nanoparticles prepared by milling soft and hard magnetic materials including Fe, Co, FeCo, SmCo, and NdFeB by surfactant-assisted ball milling. The milling parameters have been controlled carefully and nanoparticles with desired morphology have been obtained.

II. EXPERIMENTS

The starting powders had particle sizes from ~10 to 45 μm (-325 mesh). Commercially available Fe powders with 98% purity and Co powders with 99.5% purity were used. Alloy powders of Sm-Co (1:5 and 2:17), NdFeB (2:14:1), and FeCo were prepared by arc melting followed by grinding. Milling process and handling of the starting powders and the milled particles were carried out in an oxygen-free inert environment (argon gas) inside a glove box. Heptane (99.8% purity) was used as a solvent and oleic acid (90%) and oleyl amine (>98%) were used as surfactants during milling. High energy Spex 8000M mill with the milling vial and the balls made of 440C hardened steel were used for preparing the nanoparticles. The milling durations used were typically from 1 to 50 h, and ball to powder

weight ratio of 5:1 was used. The amount of surfactant used was ~10%–12% by weight of the starting powder.

Samples for magnetic measurements were prepared by embedding the nanoparticles in epoxy inside the glove box. Magnetic measurements at room temperature were performed using an alternating gradient magnetometer with measuring field up to 14 kOe, and at 5 K using a superconducting quantum interference device (SQUID) with measuring field up to 70 kOe. Structural and morphological characterizations were performed using transmission electron microscope (TEM), and x-ray diffractometer. Compositional characterizations were performed using energy dispersive x-ray and inductively coupled plasma.

III. RESULTS AND DISCUSSIONS

When surfactant was used along with heptane during milling a colored liquid (Fig. 1) was obtained along with coarse particles (referred to as slurry) which sedimented at the bottom of the milling vial. The colored liquids contained dispersion of nanoparticles smaller than 30 nm in all cases.



FIG. 1. Typical color of liquids obtained after milling without (left) and with surfactants.

^{a)}Author to whom correspondence should be addressed; electronic mail: pliu@uta.edu

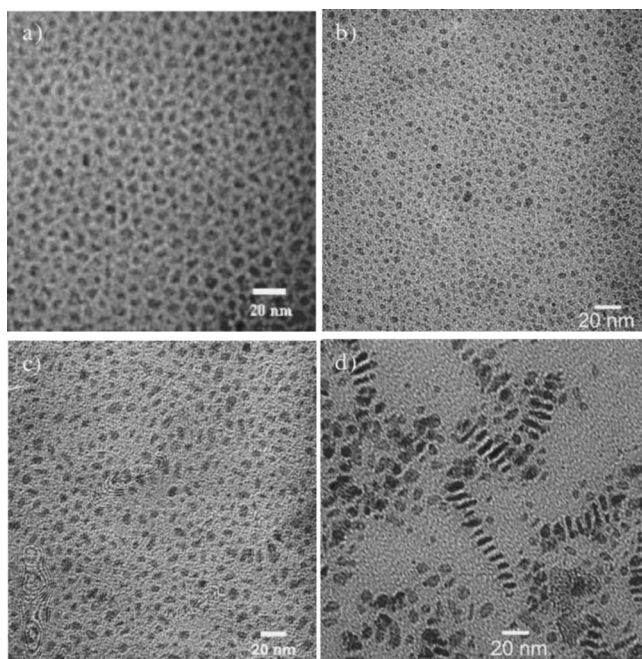


FIG. 2. TEM images of the nanoparticles prepared by milling Fe powders for: (a) 1 h and (b) 5 h, and by milling SmCo_5 -based powders for (c) 5 h and (d) 25 h.

When surfactants were not added to heptane, the solvent remained clear after milling because there were no nanoparticles dispersed in the liquid.

TEM images of the nanoparticles prepared by milling Fe powders for different durations (1, 5, 15, 25, and 50 h) using oleic acid as surfactant showed spherical or aspherical nanoparticles in sizes ranging from 3 to 9 nm [Fig. 2(a)]. There was no significant change in morphology of the nanoparticles with increase in milling time up to 50 h. Figure 2(a) shows nanoparticles with very narrow size distribution (4–6 nm) obtained by milling Fe powders obtained from a different vendor for 1 h and by using stainless steel (316 SS) balls instead of hardened steel balls. As seen in Fig. 2(a), the nanoparticles can self assemble into a regular pattern which can be achieved by controlled evaporation of the solvent after depositing the nanoparticle dispersion liquid on the TEM grid.

Similarly, TEM images of nanoparticles prepared by milling FeCo powders showed ultrafine spherical nanoparticles with a narrow particle size distribution ranging from 1.7 to 4.0 nm for samples prepared using oleic acid. The narrow size distribution and ultrafine particle sizes are the great advantages of this technique as compared with other physical methods for nanoparticle preparation.

While all the materials studied were found to be compatible with both oleic acid/oleyl amine as surfactants and heptane as solvent, only in the case of Co does oleic acid not work well with the particles. Milling of Co particles with oleic acid resulted in a jelly-like mass, not a liquid with nanoparticle dispersion, which makes separating the nanoparticles from the solution difficult. A liquid with nanoparticle dispersion could be obtained by milling with oleyl amine and the morphology of the nanoparticles showed mostly aspherical nanoparticles with a few elongated nano-

rods for the 5 h-milled sample. With increasing milling time, the percentage of elongated nanorods increased. For the sample prepared by milling for 10 h, the aspherical particles with size ranging from 2 to 8 nm were obtained. Elongated rods with width of 2–3 nm and lengths from 10 to 18 nm (aspect ratios 5–9) were also obtained. Such elongated nanostructures have not been observed in the case of nanoparticles prepared by milling Fe and FeCo powders.

The TEM images [as shown in Figs. 2(c) and 2(d)] of the nanoparticles prepared by milling SmCo_5 -based powders clearly show that the morphology of the nanoparticles varies with increased milling time. The 5 h-milled sample was found to be the nanoparticles with size ranging from 3 to 13 nm, which were mostly irregular and aspherical with a very small percentage of elongated particles. When the milling time was increased to 15 h, elongated rod-shaped nanoparticles were seen along with other irregular particles. The percentage of these nanorods increased further in the 25 h-milled sample. Typically rods with length from 7 to 20 nm and width from 3 to 6 nm were present. The aspect ratios of the nanorods varied from ~ 1.5 to 5. In addition, as shown in Fig. 2(d), the rod-shaped nanoparticles tend to align parallel to each other on the TEM grid. Similar nanorod formations were also found in the case of nanoparticles prepared by milling $\text{Sm}_2\text{Co}_{17}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based powders with oleic acid.

The mechanism of ball milling is fairly complex and does not lend itself easily to rigorous theoretical analysis due to its dynamic nature. The nanorods could be produced by fracture along some preferred crystalline orientation or anisotropic growth of the nanoparticles during the milling. Increase in the temperatures locally inside the milling vial may facilitate the growth. Materials with hexagonal- (for SmCo_5 , $\text{Sm}_2\text{Co}_{17}$, Co) and tetragonal (for $\text{Nd}_2\text{Fe}_{14}\text{B}$) structures have a preferred orientation for fracture which are the close-packed planes [(0001) for hcp], and form plate-like structures,¹¹ which upon further milling would result in the formation of elongated nanoparticles. This may also explain the absence of elongated structures in the case of Fe and FeCo which have bcc (body centered cubic) structure.

In the case of nanoparticles prepared by milling FeCo and SmCo_5 , an overall deficiency of Co was observed (for example $\text{FeCo}_{0.42}$, SmCo_1). Similarly, in the case of nanoparticles from $\text{Sm}_2(\text{CoFe})_{17}$ powders, deficiency of both Co and Fe, and in the case of nanoparticles prepared by milling $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders, deficiencies of both Fe and B (for example $\text{Nd}_2\text{Fe}_{2.12}\text{B}_{0.2}$) were observed. The possible mechanism for the deficiencies could be the phase decomposition due to the precipitation of Co/Fe/B atoms in the starting material under the impact of the balls leading to the formation of Co/Fe/B deficient phases, which has also been observed by other groups.^{12,13} The nanoparticles could be produced from different regions of the material followed by possible surfactant selective dispersion of nanoparticle species explaining the formation of nanoparticles with overall composition deficiency and inhomogeneity.

In the case of nanoparticles prepared by milling Fe, Co, and FeCo, superparamagnetic behavior was observed at room temperature. Magnetic measurements at 5 K using

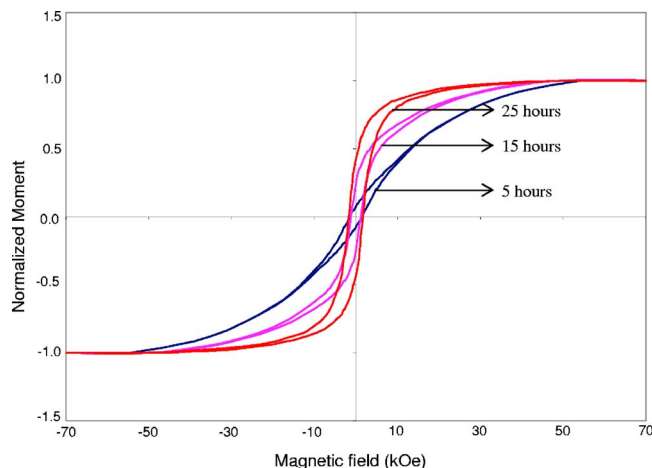


FIG. 3. Slope-corrected low-temperature (5 K) magnetization curves of nanoparticles prepared by milling SmCo_5 based powders with oleic acid for 5, 15, and 25 h (see Ref. 14).

SQUID showed some hysteresis with coercivities up to 400 Oe, and an unsaturated loop even at 70 kOe, implying a combination of superparamagnetic and ferromagnetic behavior at 5 K.

Magnetic properties of the nanoparticles prepared by milling SmCo_5 - and $\text{Sm}_2\text{Co}_{17}$ -based powders showed hysteresis at room temperature with low coercivities (<100 Oe) and very low remanence ratio (M_r/M_s) of less than 0.1. At 5 K the coercivity and the remanence ratio increased (to $H_c=1.6$ kOe, $M_r/M_s=0.42$ for SmCo_5 -based 25 h-milled samples, for instance) However, characteristic high coercivity has not been obtained which may be attributed to the composition deviation and amorphization in the nanoparticles. It is interesting to note that the remanence ratio increases with milling time. Figure 3 shows the magnetization curves of the nanoparticles by milling SmCo_5 -based powder measured at 5 K. It can be observed from the loops that M_r/M_s values increase with milling time from 0.08 for a 5 h-milled sample to 0.42 for the 25 h-milled sample. This remanence ratio enhancement with milling time at low temperatures has also been observed in the NdFeB system.

The cause for remanence enhancement could be due to the increasing percentage of elongated rod shapes and higher aspect ratios for longer milling time or the formation of most of the nanoparticles from the crystalline regions (core of the primary particle) rather than the disordered boundary regions with increasing milling time. Further investigation on the

milling time dependence of the remanence ratio and saturation magnetization is necessary to understand this effect.

IV. CONCLUSION

In summary, interesting experimental findings related to the particle size, shape, composition, and magnetic properties have been observed. Elongated rod-like nanoparticles were obtained by milling SmCo, NdFeB, and Co materials which are useful for fabrication of anisotropic nanostructured magnets. The compositions of the nanoparticles were found to deviate from that of the starting material and its optimization would be necessary. While better understanding is needed of the nanoscale mechanisms governing nanoparticle formation during surfactant-assisted ball milling of different materials, this method may become a versatile technique applicable for preparation of rare-earth based magnetic nanoparticles.

ACKNOWLEDGMENTS

This work is supported by DoD/MURI under Grant No. N00014-05-1-0497 and DoD/DARPA through ARO under Grant No. DAAD-19-03-1-0038. The authors are grateful to Dr. Jin Liu of Electron Energy Corp., and Dr. L. Li of Carpenter Technologies for providing them with the rare-earth alloy and FeCo alloy powders for this research.

¹S. S. Papell, US Patent No. 3,215,572 (1965).

²R. E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, U.K., 1985).

³S. Odenbach, *Ferrofluids—Magnetically Controllable Fluids and their Applications* (Springer, Berlin, 2002).

⁴C. Suryanarayana, *Prog. Mater. Sci.* **46**, 1 (2001).

⁵W. A. Kaczmarek, R. Bramley, A. Calka, and B. W. Ninham, *IEEE Trans. Magn.* **26**, 1840 (1990).

⁶M. N. Rahaman, *Ceramic Processing and Sintering*, 2nd ed. (Marcel Dekker, New York, 2003).

⁷K. Ono, Y. Kakefuda, R. Okuda, Y. Ishii, S. Kamimura, A. Kitamura, and M. Oshima, *J. Appl. Phys.* **91**, 8480 (2002).

⁸H. Gu, B. Xu, J. Rao, R. K. Zheng, X. X. Zhang, K. K. Fung, and C. Y. C. Wong, *J. Appl. Phys.* **93**, 7589 (2003).

⁹S. Tajima, T. Hattori, and Y. Kato, *IEEE Trans. Magn.* **30**, 3701 (1994).

¹⁰E. M. Kirkpatrick, S. A. Majetich, and M. E. McHenry, *IEEE Trans. Magn.* **32**, 4502 (1996).

¹¹G. E. Dieter, *Mechanical Metallurgy* (McGraw-Hill, Singapore, 1988).

¹²D. L. Leslie-Pelecky and R. L. Schalek, *Phys. Rev. B* **59**, 457 (1999).

¹³E. M. Kirkpatrick and D. L. Leslie-Pelecky, *J. Appl. Phys.* **87**, 6734 (2000).

¹⁴Slope correction has been made to each hysteresis curve with the assumption that the moment saturates at $\sim 80\%$ of the 70 kOe field. The curve was then normalized using its saturation moment value.