Morphological and magnetic characterization of Fe, Co, and FeCo nanoplates and nanoparticles prepared by surfactants-assisted ball milling

Narayan Poudyal, Chuan-bing Rong, and J. Ping Liu

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

(Received 24 September 2010; accepted 2 December 2010; published online 5 April 2011)

We report here the preparation of Fe, Co, and FeCo nanoplates and nanoparticles by ball milling in the presence of surfactants in organic solvents. By controlling the milling and centrifugation conditions, the Fe, Co, and FeCo nanoplates and nanoparticles with different sizes were successfully obtained, from the slurries and from the top part of the solutions, respectively. The thickness of the nanoplates is in the range of 20–200 nm and their diameter is from 5 to 30 μm. The Fe, Co, and FeCo nanoplates of about 6 nm show superparamagnetic behavior at room temperature and are ferromagnetic at low temperatures with blocking temperatures of 33, 103, and 54 K, respectively. It is found that the surfactants play multifold roles in the process.

I. INTRODUCTION

The morphology of nanomaterials can be vital in determining the materials properties.1–3 Ferromagnetic properties of a nanocrystalline ferromagnet are extremely sensitive to its shape. Ferromagnetic nanocrystals with controlled size and shape have potential applications in advanced materials and devices, such as ultrahigh-density magnetic recording media, exchange-coupled nanocomposite magnets, microwave devices, and biomedicines.4–7 Soft magnetic materials including Fe, Co, and FeCo are of special interest because of their high saturation magnetization and large permeability. A series of chemical and physical methods have been employed to fabricate Fe, Co, and FeCo magnetic nanocrystals with different morphology.8–14 Since 2006, we have adopted a surfactant-assisted ball milling method to produce magnetic nanoparticles, including rare-earth containing Sm–Co and Nd–Fe–B nanoparticles of different sizes and this method has drawn great attention recently for the fabrication of magnetic nanoparticles.15–22 Further experiments indicated that the surfactant-assisted ball milling technique is not only useful in controlling the particles’ sizes, but also their shape. In this paper, we report a facile technique for fabrication of soft magnetic Fe, Co, and FeCo nanoplates and nanoparticles by surfactant-assisted ball milling and their magnetic properties.

II. EXPERIMENTAL PROCEDURES

The starting elemental powders of particle sizes from ~10 to 45 μm are commercially available Fe with 98% purity, Co with 99.5% purity, and ~40 μm FeCo (50 at. % Fe) alloy powder prepared by arc melting followed by grinding. The starting powders were mixed with organic solvent heptane of 99.8% purity and surfactants oleic acid of 90% purity and oleylamine of 98% purity. In a typical milling load, 5 g of starting powder was mixed with 5 ml of heptane with powder-to-ball weight ratio of 1:10. The amount of surfactant used was 50% by weight of the starting powder. The mixtures were then milled using a high-energy ball milling machine for 1–20 h with hardened steel balls.

The handling of the starting materials and as-milled products was carried out in an argon gas environment inside a glovebox to protect the particles from oxidation. In this work, two different milling processes were adopted to prepare the nanocrystals: a one-step method—the starting powders were directly milled in liquids (surfactants and solvent) and a two-step method—the starting powders were first milled for 20 h without liquid first and then followed by surfactant-assisted milling. A size-selection process was employed after the milling process to obtain nanoparticles of Fe, Co, and FeCo by controlling the time of the sediment of the diluted solutions containing ball-milled particles and by controlling the centrifugal conditions.16–18 Fe, FeCo, and Co nanoplate samples were mixed with epoxy inside the glovebox to protect from oxidation and then aligned in a magnetic field of 20 kOe. The aligned sample has a disk shape with an applied magnetic field perpendicular to the plane. The magnetic properties were measured by an alternating gradient magnetometer and a superconducting interference device magnetometer. Structural and morphological characterizations were performed using x-ray diffraction (XRD) (Rigaku Ultima IV diffractometer operating with Cu Kα radiation), transmission electron microscope (TEM), scanning electron microscope (SEM), and energy dispersive x-ray (EDX) analysis.

III. RESULTS AND DISCUSSION

Figures 1(a)–1(c) show the SEM images of the one-step milled Fe, FeCo, and Co nanocrystals with a high-aspect ratio obtained after 1 h of milling. The plate-like particles with diameters in the range of 20–30 μm and thicknesses in the range of 20–200 nm (determined by high resolution SEM analysis, not shown here) were obtained. With extended...
milling time, the diameters of the nanoplates decreased significantly. For example, the average diameter of the Fe, FeCo, and Co nanoplates decreased from 25 for 1 h milling to 7 μm for 20 h milling. The surfactants play multiple roles in the milling process, including preventing cold welding of crushed particles, keeping dispersion of nanoparticles, and reducing contamination during milling. More importantly, surfactants are responsible for the formation of the high aspect-ratio nanocrystals, although the mechanism needs to be understood. It is likely related to fracture of the powder particles along some preferred crystalline orientation of the materials.

It should be pointed out that the product milled for 20 h consists of a mixture of particles with size ranging from several nanometers to micrometers. During the sediment process, the finest particles are floating at the top of the solutions. Fig. 1(d) shows the TEM images of the Fe nanoparticles that were obtained from the finest particles floating at the top. The details of the size selection process can be found in our previous work. It can be seen from the TEM images that the Fe, FeCo, and Co nanoplates have a narrow size distribution with an average size of 6 nm.

Figure 2 shows the XRD patterns of the as-prepared Fe, FeCo, and Co nanoplates and nanoparticle samples. Figure 2 also shows the XRD patterns of the Fe, FeCo, and Co nanoplates about 6 nm. It has been observed that the diffraction peaks of the Fe, FeCo, and Co nanoplates broadened and it is difficult to calculate grain size due to the low diffraction intensity, the complexity of strain state and the possible amorphization in the particles induced during the milling process.18

Magnetic properties of Fe, FeCo, and Co nanoplates and nanoparticle samples were studied by fixing the nanocrystals in epoxy under a magnetic field. Figure 3 show the demagnetization curves of Fe nanoplates measured in-plane and out-of-plane of aligned samples. The demagnetization curves measured in the out-of-plane direction deviate from the in-plane direction. The saturation and remnant magnetization are higher in-plane compared to the out-of-plane direction because of the demagnetization effect. It was found that saturation magnetization values of Fe, FeCo, and Co nanoplates obtained by ball milling for 1 h are 204, 209, and 159 emu/g, respectively; whereas the saturation magnetization values of
Fe, FeCo, and Co nanoplates obtained by milling for 20 h were 181, 167, and 121 emu/g respectively. The bulk saturation magnetization values of Fe, FeCo, and Co are reported to be 218 (Ref. 23), 235 (Ref. 24), (for Fe at. % 50), and 166 emu/g (Ref. 25), respectively.

The decrease in the magnetization of the nanoplates and nanoparticles obtained by a longer milling time might be attributed to reduction in particle size and strain, defects, and amorphization induced by high energy ball milling. The presence of surfactants on the surface of nanoplates and nanoparticles may also contribute to the actual magnetization values relatively low. The coercivity values of the Fe, FeCo, and Co nanoparticles at room temperature were found to be 50, 80, and 130 Oe, respectively, whereas the coercivity values of Fe, FeCo and Co nanoparticles obtained by milling for 20 h were 122, 238, and 356 Oe, respectively. The increase in the coercivity of the nanoplates obtained by a longer milling time might be attributed to reduction in grain size by high energy ball milling. Elemental analysis by EDX of the as-obtained FeCo nanoplates and nanoparticles showed the same stoichiometry as the starting FeCo powder (50 at. % Fe).

Figure 4(a) show hysteresis loops of Fe nanoparticles about 6 nm at 300 and 5 K. The as-prepared Fe, FeCo, and Co nanoparticles are superparamagnetic at room temperature with saturation magnetization values of 53, 67, and 42 emu/g, respectively. At 5 K Fe, FeCo, and Co nanoparticles have a coercivity value of 1.8, 4.5, and 10.7 kOe, with saturation magnetization values of 125, 137, and 78 emu/g, respectively, which are much higher than that measured at 300 K. The saturation magnetization values of 175 (Ref. 23), 215 (Ref. 26), and 55 emu/g (Ref. 27) have been obtained for the nanoparticles prepared by chemical method for Fe (7 nm), FeCo (7 nm), and Co (8 nm), respectively. The temperature-dependent magnetization was measured in a 100 Oe field between 5 and 300 K with the zero-field-cooling (ZFC) and field-cooling (FC) procedures for the Fe, FeCo and Co nanoparticles as shown in Fig. 4(b) for Fe nanoparticles. On cooling, the ZFC magnetization begins to drop and deviates from FC magnetization at blocking temperatures ($T_B$). The $M$ vs $T$ curves show peaks characteristic of a superparamagnetic transition. This study indicates that superparamagnetic behavior is blocked at 33, 54, and 103 K for Fe, FeCo, and Co nanoparticles, respectively.

IV. CONCLUSION

In summary, a facile procedure for the preparation of Fe, FeCo, and Co nanoplates and nanoparticles using the surfactant-assisted ball-milling technique has been developed. The surfactants play key roles in the processing. By controlling the milling parameters and the applying size selection process, the Fe, Co, and FeCo nanoparticles with high aspect ratios and nanoparticles with uniform sizes of 6 nm can be obtained. The plate-like Fe, Co, and FeCo particles aligned in a magnetic field showed anisotropic properties, whereas the nanoparticles of about 6 nm were superparamagnetic at room temperature.

ACKNOWLEDGMENTS

This work was supported by DoD/DARPA/ARO under Grant W911NF-08-1-0249. This work was also supported by Center of Nanostructured Materials and Characterization Center for Materials and Biology at the University of Texas at Arlington.

13L. Yan, J. Wang, X. Han, Y. Ren, Q. Liu, and F. Li, Nanotechnology 21, 095708 (2010).