



# Influence of octanoic acid on SmCo<sub>5</sub> nanoflakes prepared by surfactant-assisted high-energy ball milling

Liyun Zheng<sup>a,b,\*</sup>, Baozhi Cui<sup>a</sup>, Nilay G. Akdogan<sup>a</sup>, Wanfeng Li<sup>a</sup>, George C. Hadjipanayis<sup>a</sup>

<sup>a</sup> Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

<sup>b</sup> College of Electromechanical Engineering, Hebei University of Engineering, Handan, Hebei 056038 PR China

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## ABSTRACT

High-energy ball milling (HEBM) of magnetically hard SmCo<sub>5</sub> was conducted in heptane with octanoic acid as the surfactant. The effects of octanoic acid on the morphology and magnetic properties of the powders were investigated by scanning electron microscopy, X-ray diffraction and vibrating sample magnetometry. The results show an interesting unexpected fact that the SmCo<sub>5</sub> powders processed by octanoic acid-assisted HEBM were in form of nanoflakes with aspect-ratio of 10<sup>2</sup>–10<sup>3</sup> without the presence of nanoparticles. The thickness of nanoflakes decreases with increasing milling time. X-ray diffraction patterns did not show the sign of oxidation and the diffraction peaks of SmCo<sub>5</sub> were getting broader with the increase of milling time. The nanoflakes were magnetically anisotropic and had a higher coercivity than the micro-particles prepared by HEBM without surfactant. The coercivity of SmCo<sub>5</sub> increased initially with the milling time and then it decreased after reaching the maximum value of 15.2 kOe. High-resolution transmission electron microscopy image showed that the SmCo<sub>5</sub> nanoflakes are nanocrystalline with an average crystallite size approximately 12 nm.

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## 1. Introduction

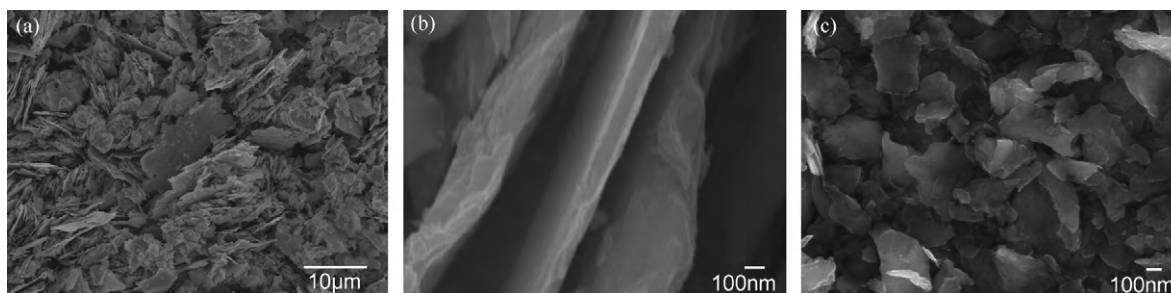
Permanent magnetic materials based on SmCo<sub>5</sub> have attracted much attention [1–4], because of their high magnetocrystalline anisotropy field  $H_A$ , high Curie temperature ( $T_C$ ) and high-energy product [(BH)<sub>max</sub>]. However, the rare-earth metals are very reactive and prone to oxidation and therefore the preparation of monodisperse rare-earth intermetallic nanoparticles has been proven to be very difficult. Great efforts have been made recently in the synthesis of rare-earth-containing nanoparticles by surfactant-assisted ball milling [5–11], which is more efficient in reducing the particle size and can prevent the natural tendency of agglomeration and cold welding processes that usually take place during regular ball milling. Kirkpatrick et al. [6] reported samarium cobalt nanoparticles prepared by ball milling using 11-phenoxyundecanoic acid as the surfactant. Their results indicated a single SmCo<sub>5</sub> phase without sign of oxidation. The SmCo<sub>5</sub> nanoparticles had an average size of 25 nm, but a broad size distribution and their coercivities were significantly reduced ( $H_c = 0.12$  T at 5 K). Another report on the preparation of SmCo<sub>5</sub> nanoparticles by ball milling used

oleic acid and oleyl amine as surfactants and produced particles with size smaller than 30 nm and with the shape of elongated rods [5]. Wang et al. produced Sm<sub>2</sub>Co<sub>17</sub> and SmCo<sub>5</sub> nanoparticles with an average size of 6–23 nm by ball milling techniques using oleic acid and oleyl amine as surfactants [10]. The coercivity was in the range of 170 Oe–3.1 kOe for Sm<sub>2</sub>Co<sub>17</sub>. Saravanan et al. also [7] synthesized highly anisotropic SmCo<sub>5</sub> nanocrystalline powders with grain size in the range 5–20 nm through the use of magnetic field-assisted milling with oleic acid. The SmCo<sub>5</sub> nanocrystalline powders obtained by this method possess unusual characteristics such as reduction in particle size, platelet-structure and high remanence values. Maximum values of  $H_{ci}$  (16 kOe),  $B_r$  (4.66 kG) and (BH)<sub>max</sub> (5.5 MGOe) were achieved for resin-bonded magnets processed with the surfactant-coated powders.

The surfactants used in all the reports mentioned above were oleic acid, oleyl amine and 11-phenoxyundecanoic acid which consist of a high number of carbon atoms [5,6,12]. Up to now, there is no report on the effect of octanoic acid as surfactant on the morphology and hard magnetic properties of novel SmCo<sub>5</sub> flakes. In this paper, we have investigated the effects of octanoic acid that has a smaller number of carbon atoms than oleic acid. We are surprised to find out an interesting fact that nearly all the SmCo<sub>5</sub> powders processed by octanoic acid-assisted ball milling were in the form of nanoflakes without the presence of nanoparticles as using other surfactants [5,6]. These nanoflakes had not only high

\* Corresponding author at: Department of Physics and Astronomy, 217 Sharp Lab, University of Delaware, Newark, DE 19716, USA. Tel.: +1 302 5595739; fax: +1 302 8311637.

E-mail address: [zheng@udel.edu](mailto:zheng@udel.edu) (L. Zheng).



**Fig. 1.** SEM images of SmCo<sub>5</sub> flakes (a) with a length of about 10 μm, (b) with a thickness ranging from 100 to 200 nm, (c) with a length of 300–500 nm after HEBM for 5 h with 15 wt.% octanoic acid.

aspect-ratio of  $10^2$ – $10^3$ , but also strong [001] texture and magnetic anisotropy.

## 2. Experimental details

SmCo<sub>5</sub> alloy was prepared by arc-melting with the appropriate excess of Sm (1.5–4 wt.% depending on the ingot weights) to compensate for the evaporation losses. The alloy was crushed, ground down to more or less equiaxed micro-particle powders with a particle size of 200 μm and milled with a SPEX 8000 M mill. The sample was milled for 3, 5, 7, 10 and 14 h with balls those were different in diameter. A ball-to-powder weight ratio of 10:1 was used. Heptane (99.8%) was used as the milling medium and octanoic acid (99%) as the surfactant. The amount of surfactant used in the high-energy ball milling (HEBM) experiments was 15, 30, 50 and 100 wt.% by the weight of the starting powder. For a comparison, the amount of oleic acid used as surfactant to ball milling SmCo<sub>5</sub> was 15 wt.%.

The structure of the milled powders was examined with a Philips 3100 X-ray diffractometer (XRD) using Cu K $\alpha$  radiation. Alignment of the milled powder samples was done in 19 kOe fields embedded in epoxy resin for XRD measurements. Morphology of the samples was investigated using a scanning electron microscope (SEM, JEOL JSM-6335F) and a transmission electron microscope (TEM, JEOL JEM-3010). Samples for TEM were prepared by letting the diluted slurry dry on carbon coated copper grids. Magnetic properties were measured with a vibrating sample magnetometer on field-aligned powder samples embedded into wax.

## 3. Results and discussions

### 3.1. Influence of octanoic acid on the morphology of SmCo<sub>5</sub>

Fig. 1 shows the SEM images of the powders milled for 5 h with 15 wt.% octanoic acid, which are taken from the slurry at the bottom of solution. It can be seen that the initial more or less equiaxed micro-particle powders became flakes with length of about 10 μm and a thickness ranging from 100 to 200 nm. The aspect ratio of these flakes reached as high as  $10^2$ . Flake prepared using wet ball milling has been known for malleable metals or alloys such as Ni, Cu, Fe-Co, but rarely for inherent brittle SmCo<sub>5</sub>. In addition, there were also some small flakes with length of 300–500 nm as shown in Fig. 1c. The upper solution was clear after HEBM with octanoic acid, which indicates that there is no nanoparticle in the upper solution. This implies that SmCo<sub>5</sub> anisotropic nanoflakes without the presence of nanoparticles can be fabricated using octanoic acid as surfactant. These results are surprising and interesting.

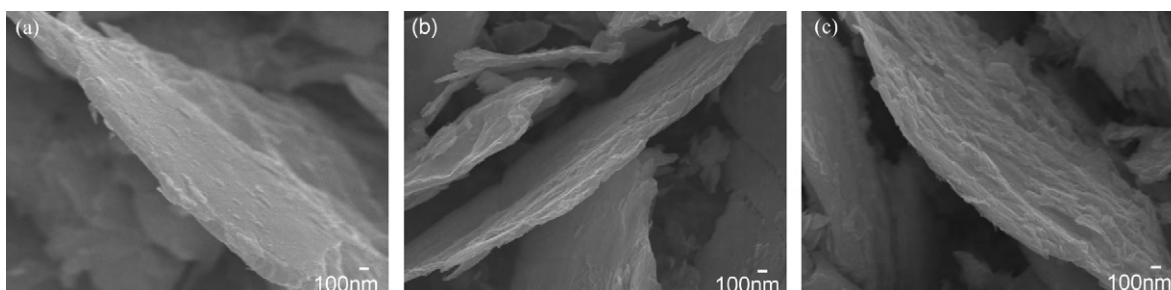
When using oleic acid as a surfactant, the dominated majority of the final product in the as-milled SmCo<sub>5</sub> powders is anisotropic nanoflakes, which is in the slurry settled down to the bottom of the solution. The thickness of nanoflakes is in the range of 8–15 nm while their length is 0.5–8 μm [12]. In the mean time, a small amount of SmCo<sub>5</sub> anisotropic nanoparticles is also formed during the surfactant-assisted HEBM process, which mainly suspend in the upper solution. In this case, the upper solution is black due to the presence of the SmCo<sub>5</sub> nanoparticles. However, the weight ratio of the nanoparticles to nanoflakes in the as-milled powders is not yet clear now.

The above results have two important implications: (i) there is no need to separate the flakes from the particles which is usually difficult to accomplish, and (ii) the flakes are more resistant to oxidation due to their smaller specific surface compare to the particles.

The SmCo<sub>5</sub> nanoflakes produced by HEBM for 5 h using the same amount of octanoic acid as surfactant were a little thicker as compared with those produced by HEBM for 5 h using oleic acid as surfactant. The reason may be that the molecular chain of octanoic acid is shorter than that of oleic acid which makes it more difficult to coat the powders than the oleic acid during the HEBM process using the same amount of surfactant.

Fig. 2 shows the SEM images of SmCo<sub>5</sub> milled for different time with 15 wt.% octanoic acid. It can be seen that most of the powder appeared as flakes with thickness about 200 nm, 50 nm and 20 nm after HEBM by 7 h, 10 h and 14 h, respectively. This indicates that increasing milling time can make much thinner flakes.

Fig. 3 shows the SEM images of SmCo<sub>5</sub> after HEBM for 5 h with different amount of octanoic acids. It can be seen that there is no clear difference among these flakes when the amount of surfactant was 30, 50 and 100 wt.%. But these flakes were thinner than those prepared using 15 wt.% surfactant (shown in Fig. 1b). This indicates that the larger amount of octanoic acid can make the flakes much thinner but has little effect on the morphology of the flakes when it exceeds 30 wt.%. It should be mentioned that HEBM of SmCo<sub>5</sub> ingots in heptane without OA resulted in the formation of magnet-



**Fig. 2.** SEM images of SmCo<sub>5</sub> flakes after HEBM with 15 wt.% octanoic acid for (a) 7 h, (b) 10 h and (c) 14 h.

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