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Influence of octanoic acid on $SmCo_5$ nanoflakes prepared by surfactant-assisted high-energy ball milling

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ABSTRACT

High-energy ball milling (HEBM) of magnetically hard $SmCo_5$ 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 $SmCo_5$ powders processed by octanoic acid-assisted HEBM were in form of nanoflakes with aspect-ratio of 10^2–10^3 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 $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ nanoflakes are nanocrystalline with an average crystallite size approximately 12 nm.

1. Introduction

Permanent magnetic materials based on $SmCo_5$ have attracted much attention [1–4], because of their high magnetocrystalline anisotropy field H_A, high Curie temperature (T_c) and high-energy product [$(BH)_{max}$]. 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 $SmCo_5$ phase without sign of oxidation. The $SmCo_5$ 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 $SmCo_5$ 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_2Co_{17} and $SmCo_5$ 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_2Co_{17}. Saravanan et al. also [7] synthesized highly anisotropic $SmCo_5$ nanocrystalline powders with grain size in the range 5–20 nm through the use of magnetic field-assisted milling with oleic acid. The $SmCo_5$ 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 $(BH)_{max}$ (5.5MGOe) 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 $SmCo_5$ 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 $SmCo_5$ powders processed by octanoic acid-assisted ball milling were in the form of nanoflakes without the presence of nanopartciles as using other surfactants [5,6]. These nanoflakes had not only high

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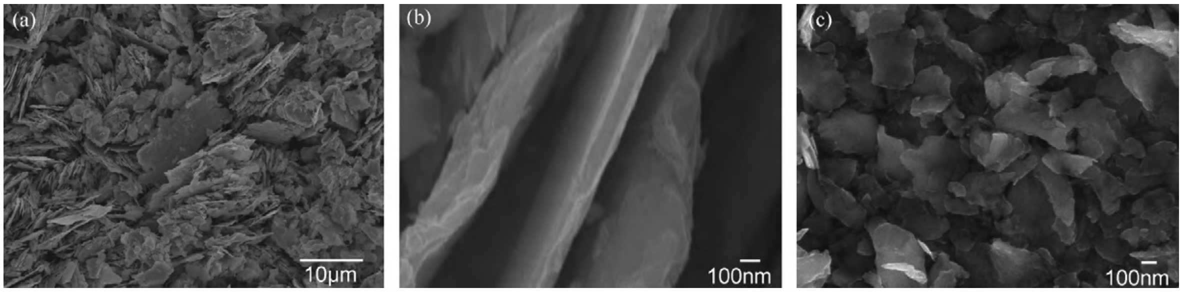

Fig. 1. SEM images of $SmCo_5$ flakes (a) with a length of about 10 μm, (b) with a thickness ranging from 100 to 200 nm, (c) with a length of 300–500 nm after HEBM for 5 h with 15 wt.% octanoic acid.

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

2. Experimental details

$SmCo_5$ 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 $SmCo_5$ was 15 wt.%.

The structure of the milled powders was examined with a Philips 3100 X-ray diffractometer (XRD) using Cu Kα 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 $SmCo_5$

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 $SmCo_5$. 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 $SmCo_5$ anisoptropic 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 $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ ingots in heptane without OA resulted in the formation of magnet-

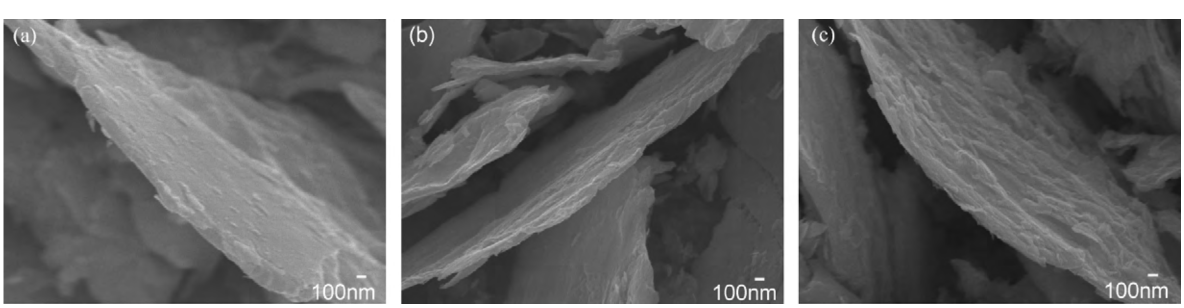

Fig. 2. SEM images of $SmCo_5$ flakes after HEBM with 15 wt.% octanoic acid for (a) 7 h, (b) 10 h and (c) 14 h.

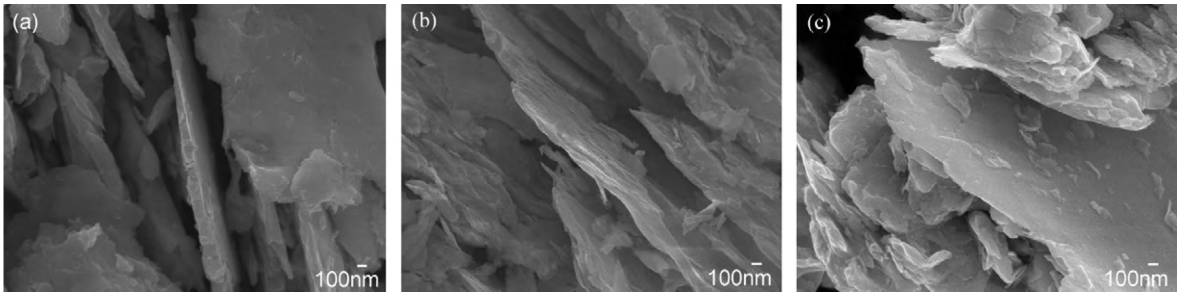

Fig. 3. SEM images of $SmCo_5$ flakes after HEBM for 5 h with (a) 30 wt.%, (b) 50 wt.% and (c) 100 wt.% octanoic acid.

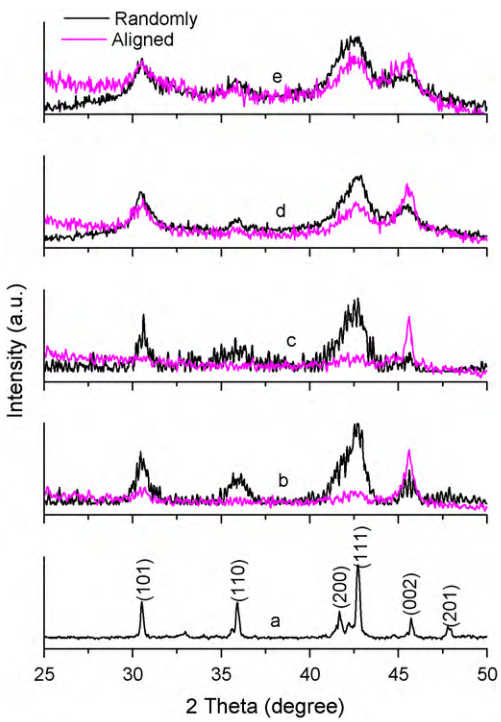

Fig. 4. The XRD patterns of the $SmCo_5$ (a) before and after HEBM for (b) 5 h, (c) 7 h, (d) 10 h and (e) 14 h with 15 wt.% octanoic acid.

ically isotropic more or less equiaxed $SmCo_5$ particles with a size of 2–30 μm [12].

3.2. Influence of surfactant on the crystal structure of $SmCo_5$

Fig. 4 shows the XRD patterns of the $SmCo_5$ before and after HEBM in heptane with 15 wt.% octanoic acid for different milling times. The XRD analysis revealed that there was no oxide peak at any stage of the milling process and all the milled powders exhibited only the $CaCu_5$ structure. The peaks of $SmCo_5$ with the hexagonal 1:5 structure get broader with the increase of milling time, which indicates that the crystallite size becomes smaller with milling time. The average crystallite size calculated via Scherrer's formula was approximately 12 nm, 10 nm, 9 nm and 9 nm and the internal strain was approximately 0.4%, 0.87%, 0.86% and 0.86% after ball milling for 5, 7, 10 and 14 h, respectively.

For the curves of (d) and (e) in Fig. 4, the diffraction peak became much broader and smaller than those in (b) and (c). This suggests that a large number of defects and dislocations formed in the flakes by plastic deformation during the HEBM. The crystalline structures may be destroyed partially when the milling time exceeded 10 h. It can also be seen that the reflection from the (0 0 2) plane was significantly enhanced when the surfactant-assisted milled for 5 h and 7 h powders were aligned in a magnetic field. After ball milling for 10 h and 14 h, the texture had been degraded to some extent.

Fig. 5 shows the high-resolution transmission electron microscopy (HRTEM) image of $SmCo_5$ after HEBM for 5 h with 15 wt.% octanoic acid. The grain size in a small piece of nanoflake is approximately 12 nm, which is consistent with the calculated results from XRD.

3.3. Influence of surfactant on the magnetic properties of $SmCo_5$

Fig. 6 shows the demagnetization curves of the $SmCo_5$ after HEBM. From Fig. 6a, it can be seen that the nanaoflakes were magnetically anisotropic. The properties of $SmCo_5$ HEBM in heptane with 15 wt.% octanoic acid for different time are shown in Fig. 6b. The coercivity of $SmCo_5$ was 14.5, 15.2, 14.5 and 9.9 kOe after HEBM for 5, 7, 10 and 14 h, respectively, which is higher than that of $SmCo_5$ ingot powders without HEBM (8.7 kOe). It can be seen that the coercivity of the $SmCo_5$ increased initially with the increase of milling time and then decreased after reaching a maximum of 15.2 kOe after ball milled for 7 h. The initial increase in coercivity is attributed to a continuous grain refinement while the decrease

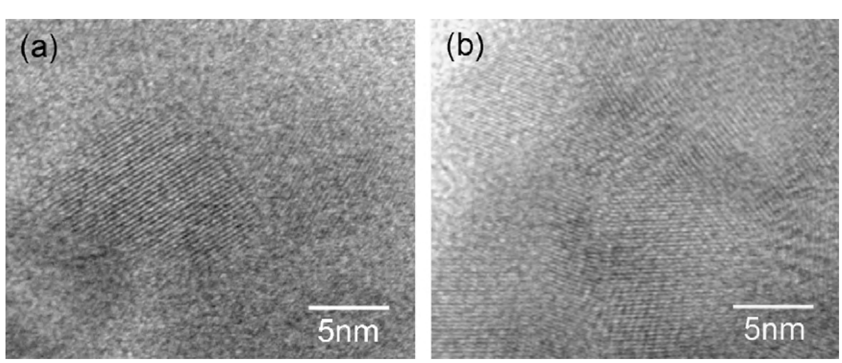

Fig. 5. HRTEM image of $SmCo_5$ flakes after HEBM for 5 h with 15 wt.% octanoic acid.

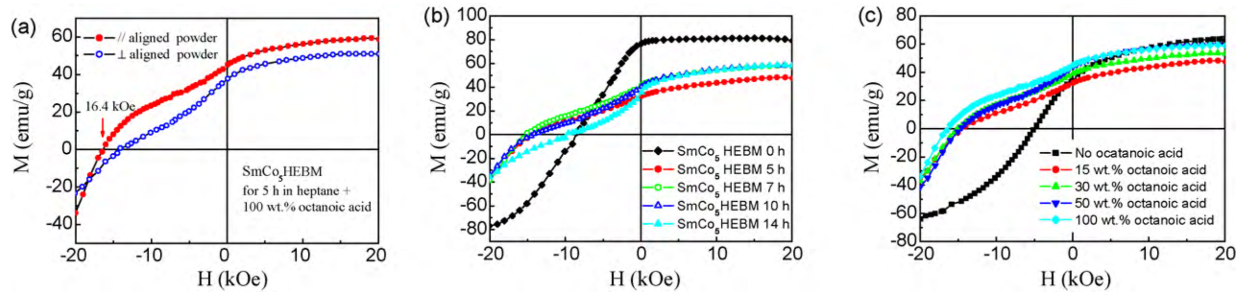

Fig. 6. Demagnetization curves of $SmCo_5$ flakes after HEBM for (a) 5 h with 100 wt.% octanoic acid, (b) different times with 100 wt.% octanoic acid and (c) 5 h with different amount of octanoic acid.

may mainly be due to the stronger exchange coupling between the finer nanocrystallines. The partially structure destruction with the further increasing of milling time may also be contributed to the decrease of coercivity.

The properties of $SmCo_5$ after HEBM for 5 h in heptane with different amount of octanoic acid are shown in Fig. 6c. It is apparent that octanoic acid-assisted HEBM led to higher coercivity than ball milling without surfactant and that the amount of octanoic acid had a little effect on the coercivity of $SmCo_5$.

4. Conclusions

We have investigated the effects of octanoic acid as surfactant on the morphology and magnetic properties of $SmCo_5$ alloy prepared by HEBM. Our study showed that octanoic acid was a good surfactant for fabricating, dispersing and oxidation-protecting nanoflakes of hard magnetic $SmCo_5$ during the HEBM process. The $SmCo_5$ powders produced using octanoic acid -assisted HEBM appeared as flakes with a thickness ranging from 20 to 200 nm and were well dispersed. The nanoflakes were anisotropic and their thickness decreased with increase of milling time. The amount of octanoic acid has little other effects on the morphology of the flakes except that a larger amount over 30 wt.% can make the flakes much thinner. The coercivities of the $SmCo_5$ nanoflakes produced using surfactant-assisted HEBM were higher than that of the microparticles with a particle size of 2–30 μm prepared by HEBM without surfactant and increased initially with increase of ball milling time and then decreased after reaching a maximum of 15.2 kOe. After a 5-h surfactant-assisted HEBM, the $SmCo_5$ nanoflakes became nanocrystalline with an average crystallite size of 12 nm.

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