Evolution of structure and magnetic properties in $PrCo_5$ magnet for high energy ball milling in ethanol*

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High energy ball milling (HEBM) is employed to produce nano-sized grains and particles. In this paper, the structure and magnetic properties are investigated in $PrCo_5$ alloy for HEBM in an ethanol milling medium. With the increase of milling time, the grain size reduces and the coercivity increases. For a milling time of less than 30 min, the hysteresis loop of the aligned sample is very different from that of the un-aligned sample and it does not show a large decrease in magnetization slope, indicating a relatively good alignment of easy axes in particles due to the fact that the texture is nearly well preserved. However, when the milling time is further prolonged, the textured structure deteriorates in the powders. Even though exchange coupling exists between grains within the particle, the magnetic properties are exchange-decoupled between particles and the dipolar interaction results in a negative value of δm in the whole range of the magnetic field.

Keywords: high energy ball milling, $PrCo_5$ magnets, alignment of easy axes, exchange coupling

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1. Introduction

The magnetic properties of nanocomposite magnets are enhanced due to the exchange coupling between nano-sized grains.[1,2] Nanostructure grains can be obtained via high energy ball milling (HEBM).[3–7] However, the ball/powder collision would deteriorate the texture and the cold welding results in a large particle size in the milling process,[3] so the easy axes are randomly oriented in particle and the magnetic properties degrade in a bulk magnet.[8] It is believed that nanoparticles may rotate freely under the action of an external field, and so the easy axes are well aligned, leading to the improvement of easy axis alignment.[1] Wet milling can prevent particles from cold-welding and agglomerating,[9,10] and the nanoparticles and nanostructure flakes are produced using the surfactants, such as oleic acid and oleyl amine, as the milling medium.[11–16] The textured structure is well preserved in a nanostructure flake, which is possibly due to the weakening of the ball/powder collision that is caused by the high viscosity of the milling medium.[11–16] Nanoparticles have a weak coercivity while textured nanostructure flakes possess a relatively high coercivity.[17] It is noted that due to the non-volatileness and the high viscosity, the cleaning of a surfactant is very difficult and the remaining surfactant causes the magnet to oxidate in a subsequent hot compaction/annealing process.[18,19] Therefore, the magnetic properties largely degrade in a bulk magnet.

Using a high-volatility solvent as a milling medium is expected to avoid the oxidation of magnetic particles because the particles are coated by the medium isolating oxygen in the milling and handling processes, and the medium is volatilized before hot compaction. A $PrCo_5$ magnet has a high magnetocrystalline anisotropy and is a potential permanent magnet candidate.[11,20] Compared with a $SmCo_5$ magnet the $PrCo_5$ magnet has a high saturation magnetization and abundant Pr in rare earth minerals.[21] In the present study, we employ the volatileness solvent of ethanol as a milling medium to produce nanosized $PrCo_5$ grains. The evolution of structure, magnetic properties, and the alignment of easy axes with milling time are systematically investigated. It is expected that these investigations could serve as a reference for preparing anisotropy permanent magnets with a nanostructure.

2. Experiment

The $PrCo_5$ alloy was prepared by arc melt pure Pr and Co in an argon atmosphere. This ingot was pulverized to particles whose size was less than 200 μm using a mortar and pestle. These powders were then put into a stainless steel vial, the mass ratio of balls to powders was 20:1, and ethanol was filled in the vial as the milling medium. HEBM was performed using a GN-2 ball milling equipment. The powders were aligned by mixing the powders with resin and they were then solidified in a magnetic field of 10 kOe (1 Oe = 79.5775 $A \cdot m^{-1}$). The phase compositions were examined by x-ray diffraction (XRD) using Cu Kα radiation. The magnetic properties were measured by

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a Lakeshore vibrating sample magnetometer (VSM) at room temperature.

3. Results and discussion

The XRD patterns of as-milled powder are displayed in Fig. 1. In the starting powder, the diffraction peaks of $PrCo_5$ phase are narrow and their intensities are strong. With a prolonged milling time, the peaks are broadened and the intensity becomes weak monotonically, indicating a reduction of grain size. For HEBM, the ball/powder collision leads to the fracture, deformation, and high dislocation density of the particles, providing the driving force of grain size reduction and a crystalline-to-amorphous phase transition.[3] The average grain sizes estimated by Jade software are 55.2 nm, 28.3 nm, 17.6 nm, 13.2 nm, and 7.5 nm for milling times of 15 min, 30 min, 60 min, 120 min, and 240 min, respectively. With an increase of the milling time, the corresponding angles of the diffraction peaks decrease a little, which is ascribed to the increases of both the strain and the lattice parameter.[11]

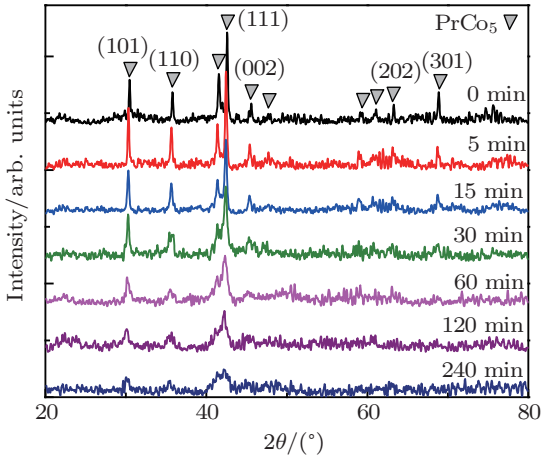


Fig. 1. (color online) XRD patterns of samples for different milling times.

To check the effect of HEBM on the magnetic properties, the hysteresis loops are measured for aligned powder ($\parallel$) and for un-aligned powder ($\circ$), respectively (see Fig. 2). The direction of the magnetic field is parallel to the aligning direction for aligned powder in the measurements. As shown in Fig. 2(h), the coercivity increases dramatically in the beginning stage for 0–30 min milling time. After milling for more than 120 min, the coercivity reaches a maximum and stays nearly unchanged. The variation of coercivity is strongly dependent on particle size and the number of interfaces. The dramatic increase of the coercivity indicates a rapid reduction of particle size; i.e., the multi-domain particles turn into single domain particles.[22] The approximate single domain size D_c is 0.245 μm, which is estimated from the formula, $D_c = 9\gamma_w/(\mu_0 M_s^2)$ (γ_w, domain wall energy density, is 35×10^{-2} J/m^2, and M_s, saturation magnetization, is 1011 kA/m).[21] But the coercivity would decrease with the further reduction of particle size to superparamagnetic size due to thermal fluctuation.[22] After milling for more than 120 min, the coercivity remains stable without decreasing, suggesting that the average particle sizes are in a range between single domain and superparamagnetic sizes. The estimated superparamagnetic size limit is 4.0 nm for $PrCo_5$ magnet, which is calculated from the formula, $D_s = (114k_BT/K_\mu)^{1/3}$[23] ($k_B = 1.38\times10^{-23}$ J/K, $T = 300$ K, and K_μ, magnetocrystalline anisotropy, is 7.6 MJ/m^3). Generally there is a multi-grain structure in powders, the powder size is larger than grain size, and some nanocrystalline grains turn into a superparamagnetic state, and even into an amorphous phase after a longer milling time. But the switch field of these particles does not decrease, which should be attributed to the multi-grain structure and the exchange coupling between crystalline and amorphous phases within the particle. As shown by the arrows, the initial magnetization increases more slowly for a longer milling time, demonstrating that the pinning effect becomes stronger due to the increase of the number of interfaces,[24] But for a milling time of 240 min, the initial magnetization increases a little rapidly, which may be ascribed to the increase of the number of soft phases, i.e., superparamagnetic or amorphous phase, resulting in the weak pinning effect on the domain wall motion. These facts about the variation of coercivity agree well with the reports of wet milling using surfactant as a milling medium.[11,16] The difference is that the coercivity increases more rapidly with the milling time in this experiment, indicating stronger effects on the reduction of powder and grain size for wet milling without a surfactant.

The degree of easy axes alignment should be investigated for the HEBM in the milling medium of ethanol. The hysteresis loops of aligned and unaligned powders are much different for a milling time less than 30 min, but are nearly the same for a milling time over 60 min (see Fig. 2). This fact suggests that for a milling time less than 30 min the crystallographic texture is nearly well preserved in particle form and that the easy axes are well aligned in the direction nearly parallel to the magnetic field direction. In order to further check the evolution of the easy axes alignment, the slope of magnetization is investigated in a field range from 18 kOe to 8 kOe (see Fig. 3). We assume that at a saturation state of magnetization, the directions of magnetic moments are all in the semisphere and tend to be parallel to the direction of the applied field. With the decrease of applied field, the magnetic moments deviate from the direction of applied field and tend to be formed along the easy axis.[25] Provided that easy axes are more randomly aligned, the slope of magnetization is larger. The magnetization is not calculated in a field range from 8 kOe to 0 kOe, considering the influence of dipolar interaction on the ratio of magnetization. As shown in the inset of Fig. 3, for a milling time of 5 min the slope of

magnetization decreases a little compared with that of starting powder without milling. In the starting particle there are possibly several different textures, and so easy axes are relatively randomly aligned in the applied field. The ball/powder collision creates an internal strain that leads to the fracture of the particles, and basically single texture exists in the smaller particle for an optimal milling time; therefore, the easy axes are well aligned and the slope of magnetization turns smaller. After milling for a long time, especially for milling over 60 min, the slope of magnetization becomes larger. We can speculate about what causes the magnetization slope to increase. On the one hand, over a prolonged milling time the textured structure deteriorates and the easy axes are oriented randomly, which happens because the large grain bands decompose into subgrains separated by low-angle grain boundaries and also because further milling leads to high angle grain boundaries and an increase of the amorphous phase.[3] On the other hand, the particle breaks up into smaller particles, even into nano-sized particles. The bulk anisotropy energy is too small in the small particle to overcome the friction for particles rotating around the applied field direction. As shown in Fig. 2, for a milling time over 60 min, the hysteresis loops are nearly the same in aligned and unaligned samples, indicating that the textured structure deteriorates and that it is hard to obtain anisotropy in the powders. It is noted that for a milling time less than 30 min, the magnetization slope largely does not decrease and the coercivity reaches 3 kOe, suggesting that the textured structure is nearly well kept in the nanostructured particles. This is different from some reports that show that the HEBM without using surfactants results in the formation of crystallographically and magnetically isotropic micro-particles that could not be oriented in a magnetic field.

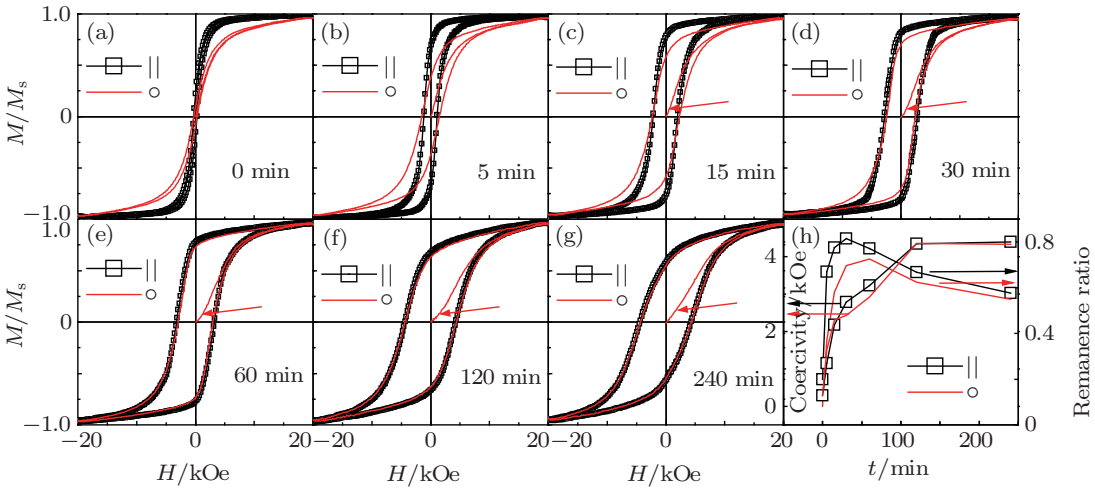


Fig. 2. (color online) Hysteresis loops of aligned and unaligned powders for milling times of 0 min (a), 5 min (b), 15 min (c), 30 min (d), 60 min (e), 120 min (f), and 240 min (g), receptively, and the variations of coercivity and remanence ratio with milling time (h).

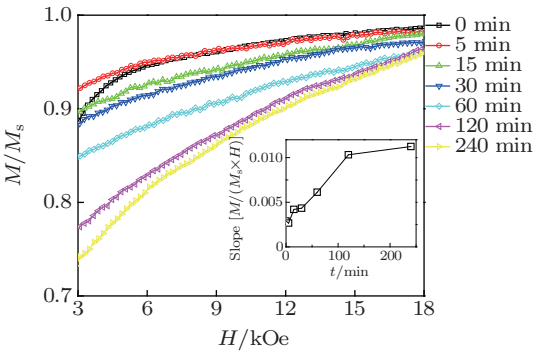


Fig. 3. (color online) Magnetization in applied field from saturation field to 3 kOe for different milling times, and the inset shows the variation of magnetization slope in the field range from 18 kOe to 8 kOe with the milling time.

The remanence ratio also increases dramatically in the beginning stage of 0–30 min milling time,; however, it decreases for a milling time over 60 min (see Fig. 2(h)). The remanence ratio is dependent on the exchange coupling between grains in nanocrystalline magnet.[26] It should be mentioned that in the unaligned powders the remanence ratio is more than 0.5 for a milling time over 60 min, indicating the existence of exchange coupling between grains.[26] Henkel plots (see Fig. 4), which are defined as $\delta m = [2M_{\rm r}(H) + M_{\rm d}(H)]/M_{\rm r} - 1$, are used to check the short range interaction of exchange coupling between atoms and long range interaction of dipolar effect in isotropic nanocrystalline magnets.[26,27] Here, $M_{\rm r}(H)$ and $M_{\rm d}(H)$ are remanences obtained by applying and subsequently removing a positive field H on thermally demagnetized sample and a negative field H on the sample magnetized to saturation, respectively. The $M_{\rm r}$ is the remanence for the sample magnetized to saturation.[27] For a diminishing exchange energy, the ferromagnetic exchange coupling leads to a parallel alignment of magnetic moments and a positive value of δm, whereas the dipolar interaction favors an antiparallel alignment of magnetic moments for reducing magnetostatic energy resulting in a negative value of δm. As shown in Fig. 4, δm value is negative in the whole range of the magnetic field, suggesting that

the dipolar interaction is larger than the exchange coupling, especially in the samples milled for 30 min and 60 min. Because of the lack of compactness in powders and no chemical bonding for jointing the particles, the magnetic properties are exchange-decoupled between particles, even though exchange coupling exists between grains within the particle. From this point of view, it is expected that hot compaction/annealing would increase the density of powders and promote the atomic interdiffusion at the surface and interface. So the exchange coupling effect could be enhanced, thereby leading to an improvement of the magnetic properties of milled powders.

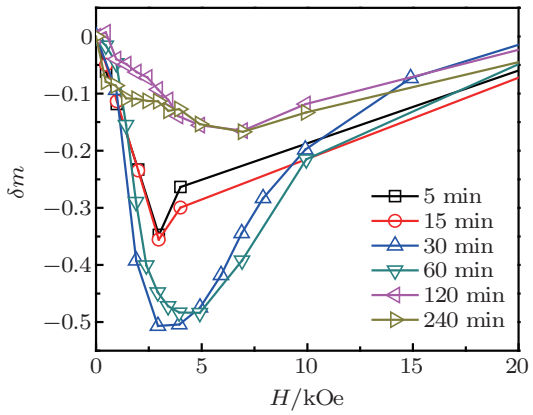


Fig. 4. (color online) Curves of δm versus H for the isotropic samples with milling times of 5 min, 15 min, 30 min, 60 min, 120 min, and 240 min, respectively.

4. Conclusions

In this study, high energy ball milling using ethanol as a milling medium results in the reduction of grain size and powder size, thereby leading to the increase of coercivity, but the textured structure would deteriorate and the easy axes are randomly oriented for a longer milling time. However, for a milling time of less than 30 min, it does not show a large decline in the alignment degree of easy axes, suggesting that the texture is nearly well preserved in particles. Further processing, such as hot compaction, is necessary to enhance the exchange coupling and improve the magnetic properties. This investigation is expected to be able to serve as a reference to the preparation of anisotropic and nano-structured magnets with high performance.

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