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Strong textured $SmCo_5$ nanoflakes with ultrahigh coercivity prepared by multistep (three steps) surfactant-assisted ball milling

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Wen-Liang Zuo, Xin Zhao, Jie-Fu Xiong, Ming Zhang, Tong-Yun Zhao, Feng-Xia Hu, Ji-Rong Sun & Bao-Gen Shen

The high coercivity of 26.2 kOe for $SmCo_5$ nanoflakes are obtained by multistep (three steps) surfactant-assisted ball milling. The magnetic properties, phase structure and morphology are studied by VSM, XRD and SEM, respectively. The results demonstrate that the three step ball-milling can keep more complete crystallinity (relatively less defects) during the process of milling compared with one step high energy ball-milling, which enhances the texture degree and coercivity. In addition, the mechanism of coercivity are also studied by the temperature dependence of demagnetization curves for aligned $SmCo_5$ nanoflakes/resin composite, the result indicates that the magnetization reversal could be controlled by co-existed mechanisms of pinning and nucleation.

Nanostructured Co-based rare earth permanent magnetic compounds with high coercivity and strong texture have drawn much attention due to their high temperature application and high performance soft/hard exchange coupled magnets[1–3]. Lately, the surfactant-assisted ball milling (SABM) method has been found efficient in the textured nanostructured rare earth compound synthesis[4]. However, the texture degree and coercivity still have much room for improvement. It is known that most of the magnetic materials are brittle when the size of the particles is large, and with the particle size decrease, the brittleness decrease and ductility increase. It is necessary to explore a higher energy to crush the sample into a small size[5,6]. Therefore, high-energy ball milling (BM) method is often used in the process for preparing the $SmCo_5$ nanoflakes[6–12], However, the high energy during the BM process may more easily destroy the crystal structure. In order to decrease the defects from BM, low-energy BM experiments were carried out for preparation nanostructured magnetic materials, and obtained excellent magnetic properties[13,14]. However, for some hard materials, low-energy is hard to crush the sample into a smaller size especially for a nano-scaled size. Therefore, a connected method of multistep (three steps) BM method is used to solve those questions. In this paper, we adopt a low-energy in the initial stage of BM, and with the decrease of powder size, the energy are concertedly increased. In the end, we find that it is a good method for preventing the destruction of crystal structure and obtaining the strong textured nanoflakes with high coercivity.

Results and Discussion

Figure 1(a) shows the demagnetization curves of $SmCo_5$ powders with the BM time from 0 to 32 h. The coercivity H_c and remanence ratio M_r/M_s dependence on BM time are also shown in the Fig. 1(b). It can be seen that both the H_c and M_r/M_s show a sharp increase in the initial stage of BM (time $\leq$ 4 h), which is mainly attributed to the grain refinement. This result demonstrates that the low-energy (30 V, 150 rpm) is effective in the grain refinement especially for the initial stage of BM. With increasing the BM

State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, People's Republic of China. Correspondence and requests for materials should be addressed to W.-L.Z. (email: wlzuo@iphy.ac.cn) or B.-G.S. (email: shenbg@aphy.iphy.ac.cn)

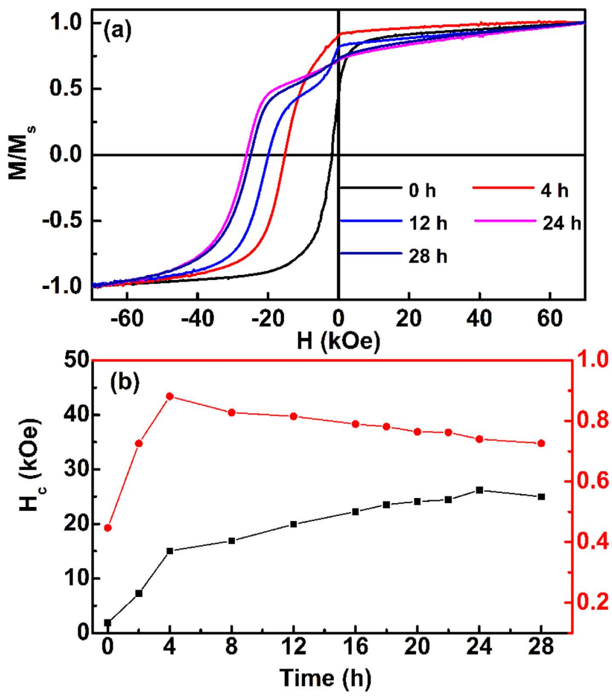

Figure 1. (**a**) The demagnetization curves of $SmCo_5$ powders with the BM time from 0 to 32 h. (**b**) The coercivity H_c and remanence ratio M_r/M_s dependence on BM time.

time and energy, H_c only shows a smooth increase and reaches a maximum value of 26.2 kOe after 24 h, which is the maximum value of coercivity for the reported rare earth permanent magnetic nanoflakes, and even higher than Tb-Fe-B[15]. Meanwhile, the decline in increase rate of coercivity can be due to the brittleness decreases and ductility increases, which lead to the decrease of grain refinement efficiency when the particle size decreases into nano-scaled[5,6]. In the end, the slight decrease of coercivity for BM 28 h indicates that the BM energy could not need to further improve. To the contrary, the M_r/M_s shows a monotonous decrease when the BM time is larger than 4 h, this phenomenon is normal and owing to multi-factor. Such as, the increase fraction of small polycrystalline nanoflakes and nanoparticles which incline to random orientation and incoherence in grain boundaries[10], the decrease uniaxial (00*l*) texture due to the plastic deformation[11]. The decrease of M_r/M_s also indicates that the high energy is harmful for forming strong textured nanoflakes. Therefore, in this paper, the maximum BM energy is no longer increase and fixed as 50 V (about 250 rpm).

Figure 2(a) shows the XRD pattern of starting $SmCo_5$ compound powder, which crystallizes primarily in the hexagonal $SmCo_5$ phase (JCPDS PD#65–4844) and with minor impurity. The XRD patterns of as-milled samples are shown in Fig. 2(b). It can be seen that the diffraction peaks become broader with increasing the BM time, which is due to the grain refinement and the introduction of the internal stress during the BM process. The average crystallite size calculated via Scherrer's formula is approximately 20 nm, 12 nm, and 6 nm, and the internal strain is about 0.16%, 0.32%, and 0.31%, corresponding to the ball milling time of 4 h, 12 h, and 24 h, respectively. Because of the relatively low BM energy, especially for 4 h milling, the broadening diffraction peaks mainly come from grain refinement. Therefore, this broadening also demonstrates that the low BM energy (150 rpm) is effective in the grain refinement. Because of the low energy instead of high energy in the initial stage of BM, the defects of crystalline structure can be decreased in the whole BM process. In addition, the XRD pattern of aligned sample (milled for 24 h) is shown in Fig. 2(c). It can be seen that the diffraction intensity of (00*l*) crystalline planes dramatically enhances whereas that of the other peaks almost disappear, suggesting that a strong (00*l*) alignment is obtained for the aligned sample (the easy magnetization directions along the *c*-axis).

Figure 3 shows the morphology evolution of nanoflakes with the BM time from 0 to 24 h. It is obviously that the start powder is irregular shape and the size are around 50–400 μm. After 4 h low energy BM (150 rpm), the start powders are crushed down to smaller particles and with the average diameter of 5 μm, which more intuitively demonstrates that the low energy is effective in the grain refinement. However, the morphology of sheet type can hardly be seen. With the increase of milling time and milling energy reach to 12 h and 200 rpm, respectively. The particles become smaller and more uniformly. Some sheet-type morphology, with micron or submicron thickness and 1–5 μm length, can be seen obviously. With further increasing milling time and energy, the $SmCo_5$ nanoflakes, with thickness about 50–200 nm and length in the range of 1–2 μm, are prepared. Furthermore, the nanoflakes form "kebab-like" morphology due to the *c*-axis texture and magnetostatic interaction, which indicates that the

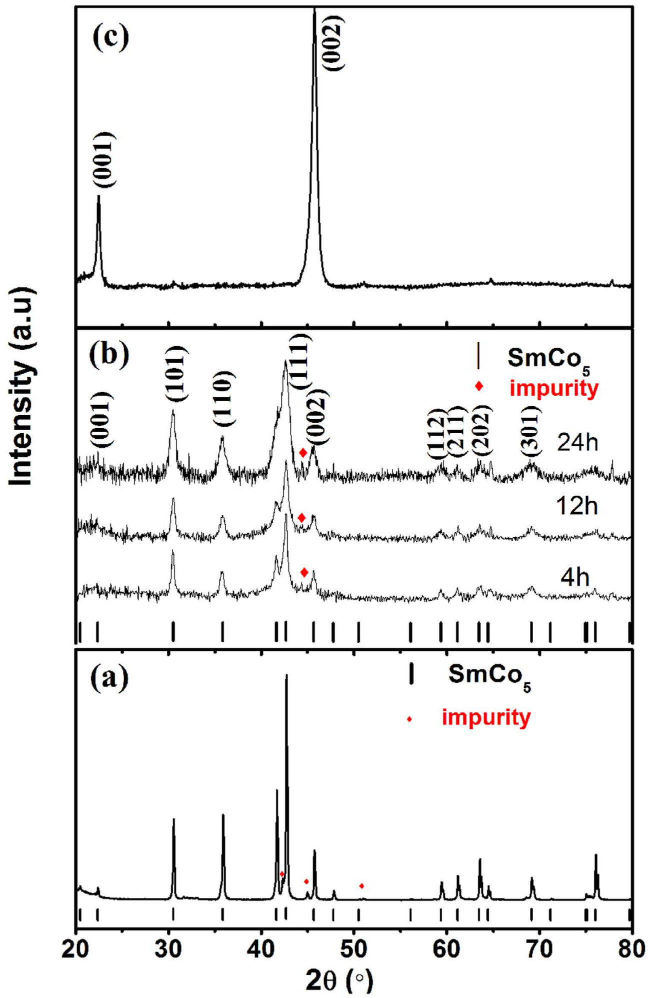

Figure 2. The XRD patterns of (a) starting $SmCo_5$ compound powder, (b) as-milled $SmCo_5$ powder with BM time from 4 to 24 h, (c) aligned sample of $SmCo_5$ nanoflakes with BM time of 24 h.

easy magnetization direction of as-milled $SmCo_5$ nanoflakes is perpendicular to the surface of the flakes. It is interesting that the nanoflakes with multistep BM shows smaller length and aspect ratio compared with those of usual one step high energy BM[6–12], which is favorable for decreasing the demagnetization fields of $SmCo_5$ nanoflakes.

Figure 4(a) shows the hysteresis loops of aligned $SmCo_5$ nanoflakes prepared by 24 h three steps SABM. The obvious anisotropy magnetic behaviors are observed. However, the H_c (24.4 kOe) for the aligned sample shows an obviously decrease compared with that of unaligned one (26.2 kOe) (see Fig. 1(a)), which phenomenon is also observed for many rare earth permanent magnetic materials[16–18]. In addition, the M_r/M_s reaches 0.94 for parallel direction of the easy axis, which indicates that the sample have a good alignment degree. In order to more accurately describe the alignment degree, we also calculate the average misalignment angle, $\varphi = \arctan[2M_r(\perp)/M_r(||)]$[7,19], where $M_r(\perp)$ and $M_r(||)$ are the remanence of perpendicular and parallel direction of the easy axis, respectively. The misalignment angle $\varphi = 19°$, which is smaller than the experiment results of BM in the magnetic field[7,20], indicates that the nanoflakes with three steps SABM have a higher texture degree.

In order to study the mechanism of coercivity for the $SmCo_5$ nanoflakes, the temperature dependence of demagnetization curves for aligned $SmCo_5$ nanoflakes/resin composite are shown in Fig. 4(b). According to the micro magnetic model, the coercivity can be generally expressed as[21–23]: $H_c = \alpha_K \alpha_\varphi 2K_1/\mu_0 M_s - N_{eff} M_s$, where K_1, N_{eff}, and M_s are the first-order anisotropy constant, the effective local demagnetization factor and the saturation magnetization, respectively. The coefficient α_K incorporates the effect of the sample microstructure, especially inhomogeneous of the intrinsic material parameters, and α_φ describes the information of the easy axis misaligned. These parameters can be determined by linear fitting $\mu_0 H_c/M_s$ against $2K_1\mu_0/M_s^2$ (See Fig. 4(b)). The temperature dependent values of K_1 and M_s are taken from the measurements of $SmCo_5$ single crystal[24]. The obtained $\alpha_K\alpha_\varphi$ and N_{eff} are 0.13 and 2.22, respectively. For the aligned samples, the $\alpha_K\alpha_\varphi$ value of 0.13 is almost entirely

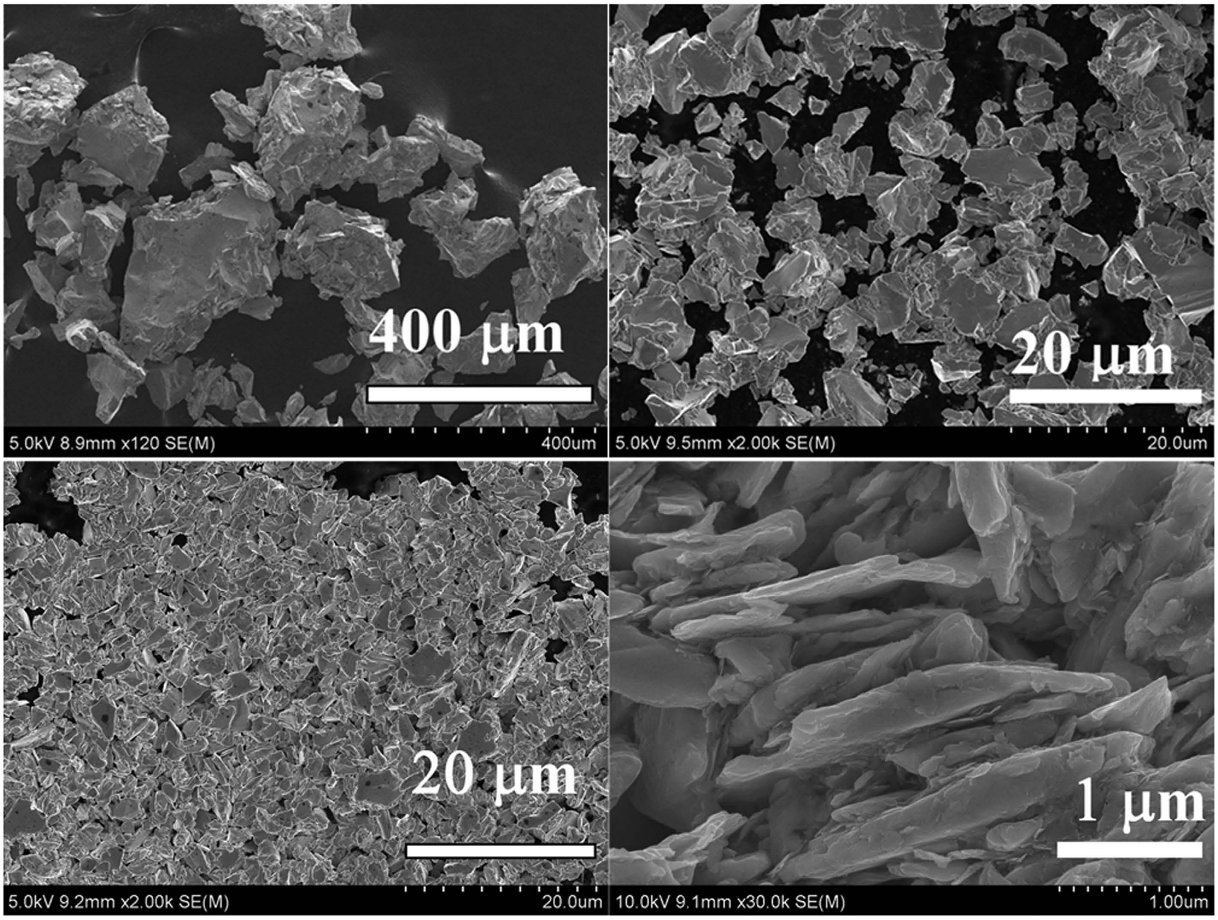

Figure 3. The SEM images of $SmCo_5$ powder with different BM time.

attributed to the microstructure parameter α_K due to the small misalignment angle, and this value is close to that of epitaxial $SmCo_5$ thin films[22], therefore, it indicate that the as-prepared nanoflakes have a similar microstructure (high textured but inhomogeneous nanocrystalline structure) compared with the epitaxial $SmCo_5$ thin films. In addition, the $\alpha_K\alpha_\varphi$ value of 0.13 also indicates that the magnetization reversal may be controlled by both nucleation and pinning ($\alpha_K < 0.3$)[22,23]. The value of N_{eff} is larger than 1 and close to the ball milled MnBi magnets[13], which indicates that large stray field could be existed in this sample except the effective local demagnetization factor. In the end, it is need to note that this paper only offer a relatively easy method (multistep BM) for preparation the nanoflakes with strong texture and high coercivity, however, it is not the optimal technological process for multistep BM. Therefore, it is need more detail experiments to develop this method.

The high coercivity of 26.2 kOe for $SmCo_5$ nanoflakes are obtained by multistep (three steps) SABM, which is the maximum coercivity of reported nanoflakes permanent materials. All the results of XRD, VSM and SEM demonstrate that the low-energy (150 rpm) is effective in the grain refinement especially in the initial stage of ball milling, however, it is need to note that low-energy is only effective in the initial stage, the higher-energy is also need for the further crush. Compared with one-step high energy BM, the three steps BM can keep more complete crystallinity during the process of milling (relatively less defects), which enhance the texture degree and coercivity. The strong textured $SmCo_5$ nanoflakes with high coercivity are very promising for future development of anisotropy nanocomposite magnets and high performance soft/hard exchange spring magnets.

Methods

$SmCo_5$ ingots were purchased from Taiyuan Tianhe Hi Tech Co Ltd. The as-obtained ingots were annealed at 1173 K for a week under vacuum, and then ground down to less than 400 μm as the starting powders. The BM experiment was performed for three steps using a GN-2 BM equipment: 4 h with the voltage of 30 V (speed is about 150 rpm); 8 h with the voltage of 40 V (speed is about 200 rpm); 16 h with the voltage of 50 V (speed is about 250 rpm). The weight ratio of balls to powders was 20:1. Oleylamine (80%–90%) and oleic acid (99%) were used as surfactants. The total amount of surfactants was 20% to the weight of the starting powders (Oleylamine and oleic acid was 1:1). Heptane (99%) was used as the carrier liquid. The aligned $SmCo_5$ nanoflakes/resin composite was prepared by mixing the as-milled

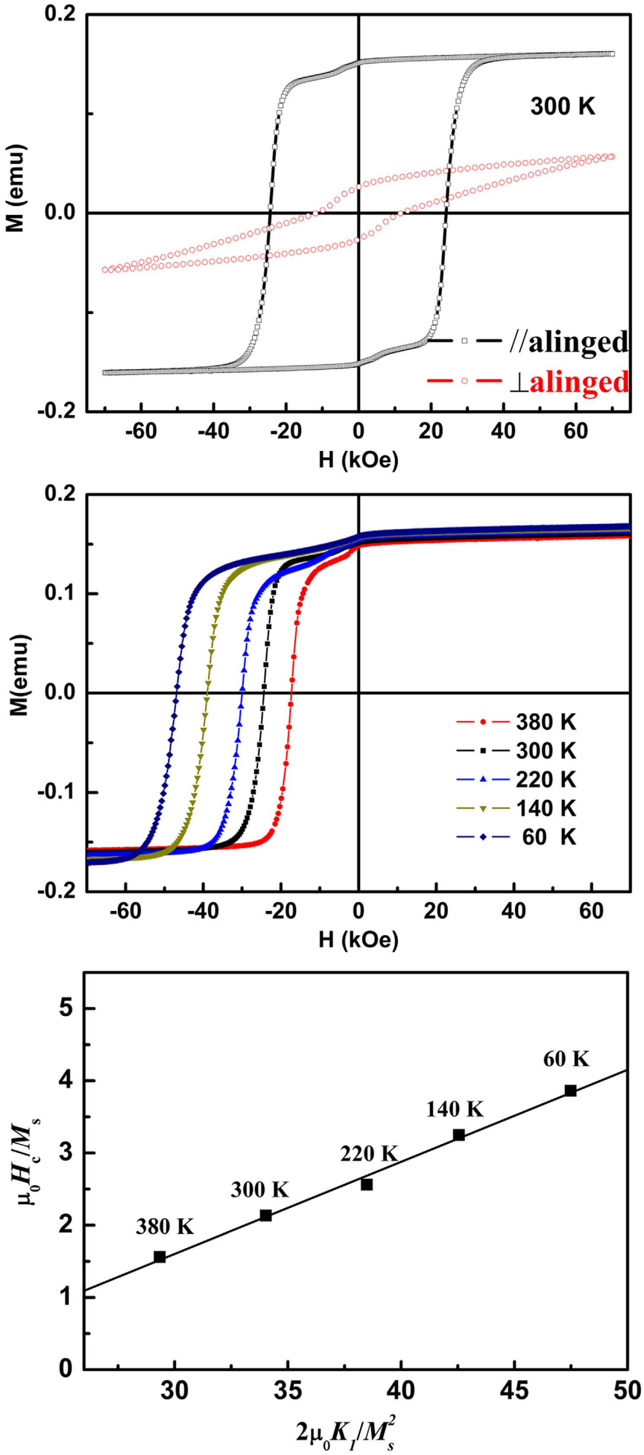

Figure 4. (**a**) The hysteresis loop, (**b**) temperature dependence of demagnetization curves and (**c**) $\mu_0 H_c / M_s$ against $2K_1\mu_0 / M_s^2$on different temperature for aligned $SmCo_5$ nanoflakes/resin composites with by 24 h BM.

nanoflakes with epoxy resin, and placing them into a 20 kOe magnetic field until the epoxy resin solidifies. The phase structure was examined by the X-ray powder diffraction (XRD) with Cu Kα radiation at room temperature. Morphology was analyzed by scanning electron microscope (SEM). Magnetic properties were measured by a SQUID VSM with the maximum field of 70 kOe.

References

1. Zeng, H., Li, J., Liu, J. P., Wang, Z. L. & Sun, S. Exchange-coupled nanocomposite magnets by nanoparticle self-assembly. *Nature* **420,** 395–398 (2002).

2. Sun, S., Murray, C. B., Weller, D., Folks, L. & Moser, A. Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices. *Science* **287,** 1989–1992 (2000).
3. Akdogan, N. G., Hadjipanayis, G. C. & Sellmyer, D. J. Anisotropic $PrCo_5$ Nanoparticles by Surfactant-Assisted Ball milling. *IEEE Trans. Magn*. **45,** 4417–4418 (2009).
4. Chakka, V. M., Altuncevahir, B., Jin, Z. Q., Li, Y. & Liu, J. P. Magnetic nanoparticles produced by surfactant-assisted ball milling. *J. Appl. Phys*. **99,** 08E912 (2006).
5. Gabay, A. M., Akdogan, N. G., Marinescu, M., Liu, J. F. & Hadjipanayis, G. C. Rare earth–cobalt hard magnetic nanoparticles and nanoflakes by high-energy milling. *J. Phys.: Condens. Matter* **22,** 164213 (2010).
6. Jiang, B. & Weng, G. J. A theory of compressive yield strength of nano-grained ceramics. *Int. J. Plast*. **20,** 2007–2026 (2004).
7. Rong, C. B., Nguyen, V. V. & Liu, J. P. Anisotropic nanostructured magnets by magnetic-field-assisted processing. *J. Appl. Phys*. **107,** 09A717 (2010).
8. Cui, B. Z. *et al.* Anisotropic $SmCo_5$ nanoflakes by surfactant-assisted high energy ball milling. *J. Appl. Phys*. **107,** 09A721 (2010).
9. Zheng, L. Y., Cui, B. Z. & Hadjipanayis, G. C. Effect of different surfactants on the formation and morphology of $SmCo_5$ nanoflakes. *Acta Mater*. **59,** 6772–6782 (2011).
10. Knutson, S. J., Shen, Y., Horwath, J. C., Barnes, P. & Chen, C. H. The effect of flake thickness on anisotropic $SmCo_5$ nanoflakes/submicronflakes with high energy product. *J. Appl. Phys*. **109,** 07A762 (2011).
11. Cui, B. Z., Li, W. F. & Hadjipanayis, G. C. Formation of $SmCo_5$ single-crystal submicron flakes and textured polycrystalline nanoflakes. *Acta Mater.* **59,** 563–571 (2011).
12. Pal, S. K., Schultz, L. & Gutfleisch, O. Effect of milling parameters on $SmCo_5$ nanoflakes prepared by surfactantassisted high energy ball milling. *J. Appl. Phys*. **113,** 013913 (2013).
13. Rama Rao, N. V., Gabay, A. M. & Hadjipanayis, G. C. Anisotropic fully dense MnBi permanent magnet with high energy product and high coercivity at elevated temperatures. *J. Phys. D: Appl. Phys*. **46,** 062001 (2013).
14. Zuo, W. L. *et al.* Textured $PrCo_5$ nanoflakes with large coercivity prepared by low power surfactant-assisted ball milling *J. Appl. Phys*. **115,** 17A728 (2014).
15. Liu, R. M. *et al.* Structure and magnetic properties of ternary Tb-Fe-B nanoparticles and nanoflakes. *Appl. Phys. Lett*. **99,** 162510 (2011).
16. Kronmüller, H., Durst, K. D. & Martinek, G. Angular dependence of the coercive field in sintered $Fe_{77}Nd_{15}B_8$ magnets. *J. Magn. Magn. Mater*. **69,** 149–157 (1987).
17. Elbaz, D. *et al.* Angular dependence of coercivity in sintered RFeB magnets. *J. Appl. Phys*. **69,** 5492 (1991).
18. Bance, S. *et al.* Influence of defect thickness on the angular dependence of coercivity in rare-earth permanent magnets. *Appl. Phys. Lett*. **104,** 182408 (2014).
19. Fernengel, W., Lehnert, A., Katter, M., Rodewald, W. & Wall, B. Examination of the degree of alignment in sintered Nd-Fe-B magnets by measurements of the remanent polarizations. *J. Magn. Magn. Mater*. **157/158,** 19–20 (1996).
20. Poudyal, N., Nguyen, V. V., Rong, C. B. & Liu, J. P. Anisotropic bonded magnets fabricated via surfactant-assisted ball milling and magnetic-field processing. *J. Phys. D: Appl. Phys*. **44,** 335002 (2011).
21. Kou, X. C., Kronmüller, H., Givord, D. & Rossignol, M. F. Coercivity mechanism of sintered $Pr_{17}Fe_{75}B_8$ and $Pr_{17}Fe_{53}B_{30}$ permanent magnets. *Phys. Rev. B* **50,** 3849 (1994).
22. Singh, A. *et al.* Mechanism of coercivity in epitaxial $SmCo_5$ thin films. *Phys. Rev. B* **77,** 104443 (2008).
23. Kronmüller, H. & Durst, K. D. Analysis of the magnetic hardening mechanism in RE-FeB permanent magnets. *J. Magn. Magn. Mater*. **74,** 291–302 (1988).
24. Frederick, W. G. D. & Hoch, M. Magnetic properties of single crystal $Nd_{1-x}Sm_xCo_5$ alloys. *IEEE Tran. Magn*. **12,** 1434–1436 (1975).

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Author Contributions
Conceived and designed the study and experiments: W.L.Z. and B.G.S. Performed the experiments: W.L.Z. and X.Z. Analyzed the data: W.L.Z., X.Z., J.F.X., M.Z., T.Y.Z., F.X.H., J.R.S. and B.G.S. Wrote the paper: W.L.Z. and B.G.S. All authors discussed the results and commented on the manuscript.

Additional Information
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