INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **37** (2004) L45–L48 PII: S0022-3727(04)87180-8

RAPID COMMUNICATION

Field-ball milling induced anisotropy in magnetic particles

Narayan Poudyal[1], Baki Altuncevahir[1], Vamsi Chakka[1], Kanghua Chen[1], Truman D Black[1], J Ping Liu[1], Yong Ding[2] and Zhong Lin Wang[2]

[1]Department of Physics, University of Texas at Arlington, Arlington, TX 76019, USA
[2] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

E-mail: pliu@uta.edu

Received 1 October 2004, in final form 1 November 2004
Published 2 December 2004
Online at stacks.iop.org/JPhysD/37/L45
doi:10.1088/0022-3727/37/24/L01

Abstract
$Nd_2Fe_{14}B$ and Sm_2Co_{17} particles of submicrometre sizes have been prepared by ball milling in a magnetic field. Structural and magnetic characterization reveal that these submicrometre particles milled in a magnetic field, consisting of nanosize grains, exhibit strong magnetic anisotropy compared with the particles milled without a magnetic field. Based on *in situ* observations of the field-ball milling in a transparent container, the mechanism of field-induced anisotropy in the nanostructured hard magnetic particles is discussed.

Nanocomposite hard magnetic materials have drawn considerable attention for their potential for very high energy products [1–3]. However, this potential can be realized only if the nanosize grains of the hard magnetic phases can be aligned to form desired textures in the materials. It turns out to be a significant challenge to fabricate nanostructured bulk magnets with texture. The difficulties in achieving the alignment originate from the strong inter-particle reactions and reduced anisotropy of the particles, as well as the low thermal stability of the nanoparticles. Very fine ferromagnetic nanoparticles may have a superparamagnetic behaviour. They are also easy to agglomerate or be contaminated by oxygen and other reactive elements. As a consequence of these difficulties, hard magnetic nanoparticles can hardly be aligned using an electromagnet as in the situation for sintered bulk magnets of microsize hard magnetic powder particles. Other techniques for producing anisotropic bulk magnets such as hot pressing are associated with long thermal exposure and can cause excessive grain growth. For these reasons, assemblies of magnetic nanoparticles and nanostructured bulk magnets are generally magnetically isotropic. One of the possible approaches to producing anisotropic bulk nanocomposite magnets is to fabricate anisotropic micrometre sized or submicrometre sized particles containing aligned nanosized grains in the particles so that anisotropic bulk magnets can be made from the particles. In this letter we report our recent experiments in preparing anisotropic hard magnetic particles with nanosized grain structures by ball milling in a magnetic field.

Ball milling is an effective technique for producing mechanically alloyed materials and powder particles [4, 5]. In recent years ball milling has been widely applied to preparing nanostructured hard magnetic powder particles because with this technique one can produce powder particles of a very fine particle size and grain size [6, 7]. Combined with subsequent heat treatments, a controlled nanostructure can be obtained in the particles. However, as mentioned above, the nanostructured powder particles produced in ordinary ball milling are generally magnetically isotropic. The motivation of this investigation was based on the possible alignment effect of an external magnetic field on field-ball milled particles.

$Nd_2Fe_{14}B$ and Sm_2Co_{17} based coarse powders ($\sim$ mesh 325) were obtained by pulverizing ingots. The grain size in the ingot is of the order of tens of micrometres. The powders were then ball milled in a magnetic field (>3 kOe).

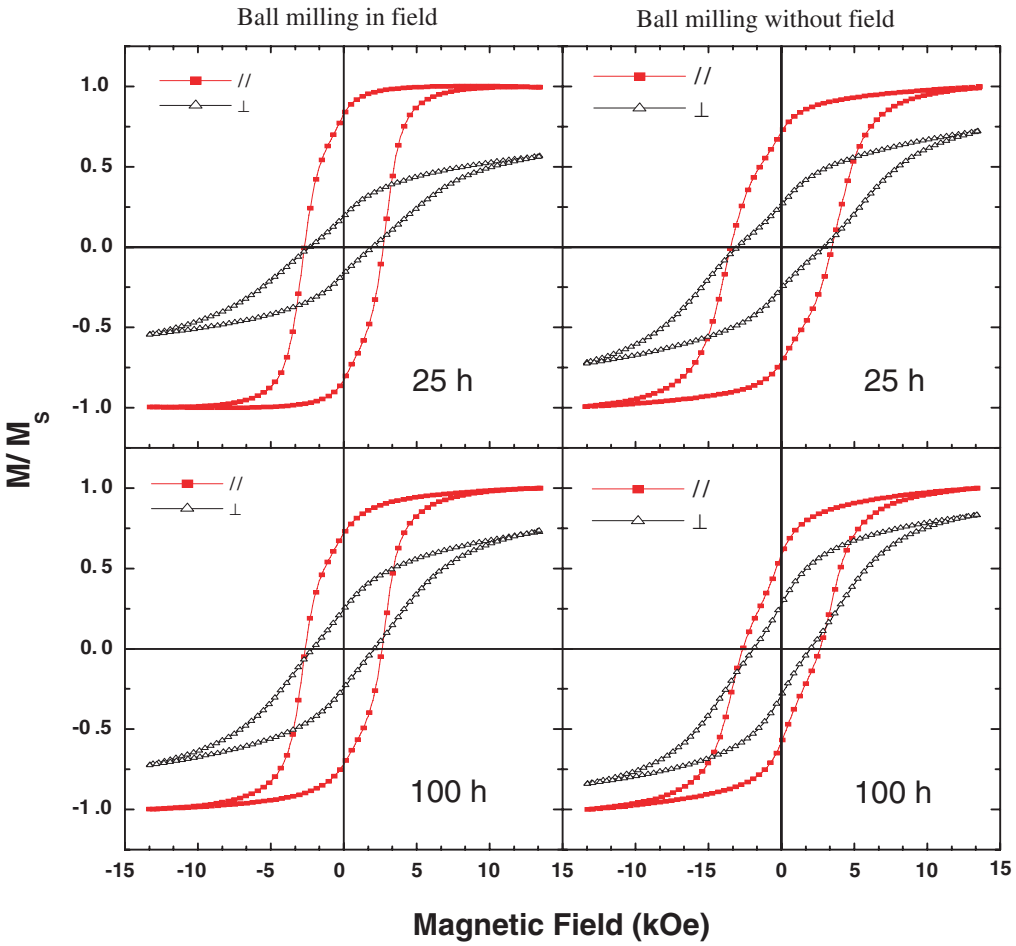

Figure 1. Magnetic hysteresis loops measured in both the alignment direction (easy magnetization direction) and the direction perpendicular to the easy direction of $Nd_2Fe_{14}B$ powder samples aligned in solidified epoxy. The left column has loops of the powders milled in a magnetic field and the right column has loops of the powders milled without a magnetic field.

(This figure is in colour only in the electronic version)

The balls and vial were made of non-magnetic stainless steel. The balls were about 1 cm in diameter. The ball-to-powder weight ratio was 30. The milling was carried out for up to 100 h in Vertrel XF solvent or mineral oil, and the powders were sampled every 25 h. The sampled powders were aligned in a magnetic field of 6–7 kOe in hardening epoxy. The magnetic properties of aligned powder samples were measured by using an alternating gradient force magnetometer (AGFM) and a superconducting quantum interference device (SQUID) magnetometer at room temperature. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to characterize the structure of the powders. A Nanotrac laser particle size analyser was used to measure the particle size as well. For comparison, the powders were also milled under the same conditions without a magnetic field.

On comparing the magnetic hysteresis loops of the $Nd_2Fe_{14}B$ powders milled in a magnetic field with those milled without a magnetic field, it is striking to observe that the remanent magnetization to saturation magnetization ratio (M_r/M_s) for the field-milled samples is remarkably higher than for those milled without the field. The increase in the M_r/M_s ratio upon field milling is in the range from 15% to 24% (measured in the easy magnetization direction). The increased M_r/M_s ratio indicates an enhanced anisotropy of the particles. To understand this point better, we also measured the hysteresis loops in the hard magnetization direction (perpendicular to the alignment direction). Figure 1 shows the loops measured in both the easy and the hard directions of the samples (only loops for samples prepared for 25 and 100 h were plotted here). It can be clearly seen that samples milled in the field have higher anisotropy than those milled without an applied magnetic field. It is evident that the powders milled in a magnetic field have enhanced magnetic anisotropy.

SEM and TEM observations were made along with the magnetic characterization of the particles. It was found that the particle size reduces rapidly in the early hours of the milling, in both the field-ball milling and non-field-ball milling. The average size reaches its minimum after about 25 h and remains unchanged with further milling. In our experiments, the minimum average size was about 100 nm. It is important to note that the particles size is not equal to the grain size. The grain size, starting with the original particle size of tens of micrometres, reduces to nanometric order with milling. Figure 2 is a TEM image of a $Nd_2Fe_{14}B$ submicrometre particle milled for 25 h in a magnetic field in Vertrel solvent.

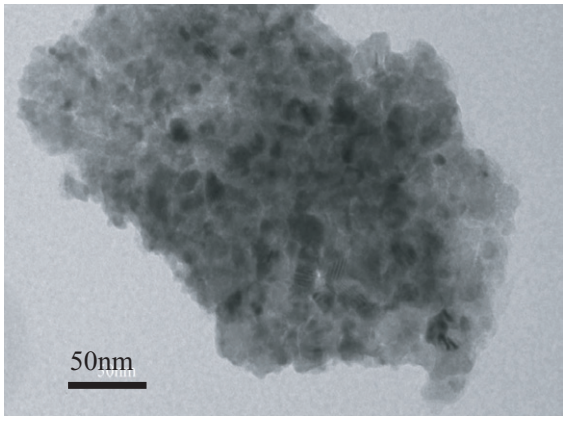

Figure 2. TEM image of an $Nd_2Fe_{14}B$ particle field-milled for 25 h in Vertrel XF solvent.

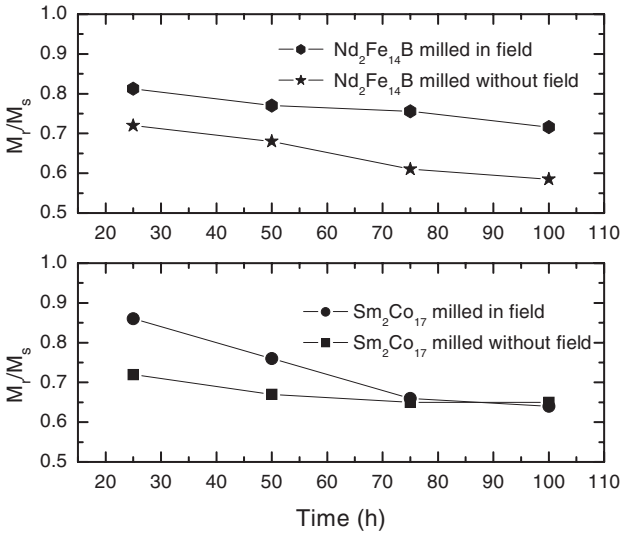

Figure 3. Values of M_r/M_s of $Nd_2Fe_{14}B$ samples and Sm_2Co_{17} samples plotted versus milling time.

It is clearly seen from this figure that the particles contain many grains smaller than 50 nm. Samples milled without an applied field show a similar morphology. The average grain size is about 20 nm. The small grains inside a particle are formed either from plastic deformation of the particles during milling or from joining (welding) of small nanoparticles. The joining (welding) of small first-degree nanoparticles into larger second-degree particles is an important process in ball milling. Our laser analyser measurements revealed that there were a considerable number of nanosized particles in the liquid after the ball milling even though the average size never reached nanometric order. After milling for a certain time the crushing and the welding reached an equilibrium, and the average particle size remained unchanged with further milling. Eventually an amorphous structure will be created with further milling in the particles due to the severe plastic deformation.

The reduced particle size and grain size resulting from severe plastic deformation lead to the monotonic reduction of the M_r/M_s ratio with milling time because of the reduced magnetic anisotropy. It should be noted from figure 1 that samples milled without a magnetic field still possess some magnetic anisotropy. This is not strange because some large particles in the powders can still be aligned in epoxy with a magnetic field, while small particles can only be aligned when they are joined together to form larger anisotropic second-degree particles. When the milling time was longer than 100 h, the anisotropy was dramatically reduced or essentially vanished, depending on the amorphization of the particles observed through the XRD and TEM measurements.

Field-induced anisotropy during ball milling has also been observed in Sm_2Co_{17} powder samples. Figure 3 shows the milling time dependence of the M_r/M_s ratio of $Nd_2Fe_{14}B$ and Sm_2Co_{17} samples milled with and without a magnetic field. It is interesting to note that the difference between the M_r/M_s ratios of field-milled samples and non-field-milled samples tends to be larger with increasing milling time in the case of $Nd_2Fe_{14}B$, while in the case of Sm_2Co_{17} the difference becomes smaller (it vanishes at 100 h). This is attributed to the difference between these two materials in their amorphization that leads to a reduction in magnetic anisotropy, and our XRD results are consistent with the magnetic measurements.

We made careful observations and analyses by SEM, XRD and TEM of the field-ball milled and non-field-ball milled particles and found no considerable difference in the particle size and grain size, which excludes the possibility that the difference in the magnetic anisotropy was caused by a difference in the particle size or grain size. From figure 2 we have seen that each particle contains hundreds of grains which normally align randomly in the particles in order to reduce the static magnetic energy.

To understand the mechanism of the field-induced anisotropy in the powder particles, we used a transparent vial to observe the powder and ball motion behaviour during milling. It was interesting to see that in the presence of a magnetic field the powder particles form chains along the field direction. The dimensions of the chains were a few centimetres in length and a few millimetres in diameter. The particles inside the chains were aligned. While the chains are colliding with the balls, re-joined small particles preferentially align themselves along the chain's long axis direction, which is normally parallel to the magnetic field direction. Without a magnetic field, the smaller particles naturally join the larger particles with their easy magnetization directions in a random way to reduce the magnetic static energy. In the presence of a magnetic field, in an ideal situation, each final 'second-degree particle' will be a short 'chain' of many nanosized particles. This will result in anisotropic micrometre or submicrometre particles.

To verify whether the nanosized grains are aligned in the powder particles milled in a magnetic field, we carried out XRD measurements of aligned powder samples of the $Nd_2Fe_{14}B$ materials milled with and without a magnetic field for 100 h (figure 4). The patterns (a) and (b) were from samples hardened in epoxy without an applied magnetic field and so we did not see any alignment. On comparing the patterns (c) and (d), it is evident that the field-milled samples (even their grain sizes are very fine after being milled for 100 h) have a very good *c*-axis (the easy magnetization direction) alignment. Pattern (c) shows a much stronger reflection intensity of the *c*-axis planes (the x-ray patterns (c) and (d) were measured under the same

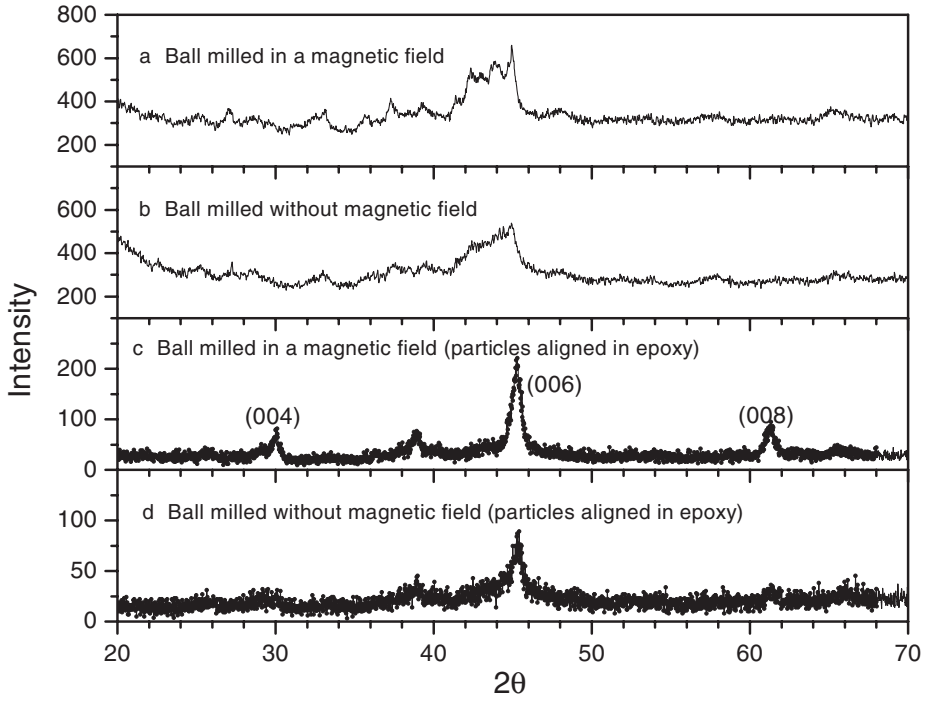

Figure 4. XRD patterns of $Nd_2Fe_{14}B$ powder samples milled for 100 h.

condition). The non-field-milled powders had a low degree alignment due to the existence of some large size grains and particles in the powders; however, the intensity of the (006) peak is substantially weaker than that in pattern (c), and other peaks in the *c*-axis are not recognizable. Considering the possible misalignment in the epoxy bonded magnetic particle specimens, pattern (c) shows a strong texture in the field-milled particles. A simple estimation of the anisotropic field by extrapolation of the loops in figure 1 for the 100 h field-milled samples gives a value of 4.5 T at room temperature (with error bar ∼20–30%), which is of the same order of the value of 7.3 T for $Nd_2Fe_{14}B$ single crystals [8, 9]. If we include the reduced anisotropy due to the reduced particle size and grain size, this value of 4.5 T is a sign that most nanosized grains and particles are quite well aligned and therefore the submicrometre particles are strongly anisotropic. This is consistent with the texture observed from the XRD results.

There may be other mechanisms causing this field-milling-induced anisotropy in the hard magnetic particles. For instance, the enhanced M_r/M_s ratio in the field-milled samples may also originate from the improved inter-grain exchange coupling. The details need to be investigated further.

In summary, magnetic field milling shows promise for producing nanostructured anisotropic hard magnetic particles. These nanostructured anisotropic submicrometre particles can be used for fabricating anisotropic bulk nanocomposite magnets. We have noticed that magnetic field milling was adopted to improve the energy product of bonded single-phase $Nd_2Fe_{14}B$ magnets [10]. We are currently working to extend this technique to producing nanocomposite anisotropic powder particles and bulk magnets. The results will be reported elsewhere.

Acknowledgments

This work is supported by DARPA through ARO under grant DAAD 19-03-1-0038. The authors thank Dr J F Liu at EEC Corporation and Dr L Li at Carpenter Inc. for their offer of the raw materials.

References

[1] Coehoorn R, de Mooij D B and de Waard C 1989 *J. Magn. Magn. Mater.* **80** 101
[2] Skomski R and Coey J M D 1993 *Phys. Rev.* B **48** 15812
[3] Zeng H, Li J, Liu J P, Wang Z L and Sun S 2002 *Nature* **420** 395
[4] Lu L and Lai M O 1998 *Mechanical Alloying* (Boston, MA: Kluwer)
[5] Suryanarayana C 2001 *Prog. Mater. Sci.* **46** 1–184
[6] McCormick P G 1997 *Handbook on the Physics and Chemistry of Rare Earths* ed K A Gschneidner Jr and L Eyring (BV, Amsterdam: Elsevier) pp 47–81
[7] Venkatesan M, Jiang C and Coey J M D 2002 *J. Magn. Magn. Mater.* **242–245** 1350
[8] Givord D, Li H S and Perrier del a Bathie R 1984 *Solid State Commun.* **51** 857
[9] Sagawa M, Fujimura S, Yamamoto H, Matsuura Y and Hyrosawa S 1985 *J. Appl. Phys.* **57** 4094
[10] Akira M, Osamu Y and Tetsuji S 2000 *Japanese patent*—195712