AIP Applied Physics Letters

Coercivity and squareness enhancement in ball-milled hard magnetic–antiferromagnetic composites

J. Sort, J. Nogués, S. Suriñach, J. S. Muñoz, M. D. Baró, E. Chappel, F. Dupont, and G. Chouteau

Citation: Applied Physics Letters **79**, 1142 (2001); doi: 10.1063/1.1392308
View online: http://dx.doi.org/10.1063/1.1392308
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/79/8?ver=pdfcov
Published by the AIP Publishing

Coercivity and squareness enhancement in ball-milled hard magnetic–antiferromagnetic composites

J. Sort, J. Nogués, S. Suriñach, J. S. Muñoz, and M. D. Baró[a)]
Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain

E. Chappel, F. Dupont, and G. Chouteau
Grenoble High Field Laboratory, B.P. 166, Grenoble 38042, Cedex 9, France

(Received 28 March 2001; accepted for publication 14 June 2001)

The room-temperature coercivity, H_C, and squareness, M_R/M_S (remanence/saturation magnetizations), of permanent magnet, $SmCo_5$ powders have been enhanced by ball milling with antiferromagnetic NiO (with Néel temperature, $T_N = 590$ K). This enhancement is observed in the as-milled state. However, when the milling of $SmCo_5$ is carried out with an antiferromagnet with T_N below room temperature (e.g., for CoO, $T_N = 290$ K), the coercivity enhancement is only observed at low temperatures after field cooling through T_N. The ferromagnetic–antiferromagnetic exchange coupling induced either by local heating during milling ($SmCo_5$+NiO) or field cooling ($SmCo_5$+CoO) is shown to be the origin of the H_C increase. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1392308]

During the last few decades permanent magnet development has been centered on the production of highly anisotropic materials[1] and nanocomposite magnets consisting of a mixture of exchange coupled hard and soft magnetic components, commonly known as spring magnets.[2] In the latter, a remanence enhancement is induced by the ferromagnetic (FM)–ferromagnetic exchange interaction. However, usually in these systems a reduction of coercivity, H_C, cannot be avoided.[2] Conversely, an enhancement of H_C and a shift of the hysteresis loops along the field axis (exchange bias) are well known effects of antiferromagnetic (AFM)–FM exchange coupling.[3,4] Exchange bias has been extensively studied in thin films, because of its role in spin-valve devices.[5] However, the coercivity enhancement associated with exchange bias has been investigated less.[6] In the case of powders, usually a widening of the loop is observed far below room temperature (RT), either because the Néel temperature, T_N, of the AFM is below RT or the AFM grains are so small that they behave superparamagnetically at RT.[3,4,7,8] Furthermore, in powders, the AFM phase is usually obtained by oxidation or sulfuration of the FM (e.g., Co–CoO, Fe–FeS or Ni–NiO).[3,4,7,8] In the case of rare-earth permanent magnets (e.g., $SmCo_5$ or $Nd_2Fe_{14}B$) in general it is not possible to obtain AFM phases by oxidation, since it is mainly selective for rare-earth and the oxides obtained (e.g., Sm_2O_3 or Nd_2O_3) are not antiferromagnetic. However, it has been demonstrated recently that it is possible to induce FM–AFM coupling when FM and AFM powders are milled together.[9,10] In this letter we report the enhancement of H_C and M_R/M_S in $SmCo_5$ due to AFM–FM exchange interactions when ball milled with NiO and CoO.

Powders of $SmCo_5$ (99%, <500 μm)[11] were milled alone or together with NiO (99%, <44 μm) and CoO (99%, <44 μm) in a weight ratio of 1:1. Note that NiO and CoO are antiferromagnets with $T_N = 590$ and 290 K, respectively. The milling was carried out for different times (0.25–32 h) using a planetary mill.[10]

The microstructure of the as-milled powders was studied by x-ray diffraction (XRD). XRD patterns were fitted using the Rietveld method from which the crystallite size, $\langle D \rangle$, was evaluated for each component. Morphological characterization was performed using a scanning electron microscope (SEM). Magnetic hysteresis loops of tightly packed isotropic powders were carried out at RT with a maximum field of $\mu_0 H_{max} = 23$ T, by means of an extraction magnetometer. Hysteresis loops after zero-field cooling (ZFC) and field cooling ($\mu_0 H_{FC} = 5$ T) of $SmCo_5$ and $SmCo_5$+CoO were also carried out at $T = 30$ and 100 K.

For the three systems studied ($SmCo_5$, $SmCo_5$+NiO and $SmCo_5$+CoO) the $SmCo_5$ crystallite size, $\langle D \rangle$, is a decreasing function of the milling time, especially during the first 4 h of milling. However, this reduction is somewhat steeper when milling $SmCo_5$ alone. For long milling times the crystallite size stabilizes to a nanometric range (e.g., $\langle D \rangle = 10$ nm in $SmCo_5$+CoO), but $\langle D \rangle$ remains larger in $SmCo_5$+CoO and $SmCo_5$+NiO than in $SmCo_5$ alone.

SEM micrographs of ball-milled $SmCo_5$ also reveal a reduction of the particle size and changes in shape with an increase in the milling time, from about 500 μm irregular and sharp-edged particles to roughly spherical particles of about 5 μm in the 32 h ball-milled $SmCo_5$. A different microstructure is encountered in ball-milled $SmCo_5$+NiO and $SmCo_5$+CoO. In both cases, in addition to the $SmCo_5$ particle size reduction, observed in $SmCo_5$ alone, the $SmCo_5$ particles in $SmCo_5$+AFM become progressively surrounded and soldered to NiO or CoO. After 32 h of milling they form aggregates of up to 10 μm in size composed of several $SmCo_5$ particles embedded in a NiO or CoO "matrix."

Shown in Fig. 1 is the milling time dependence of the coercivity, H_C, for the three series of powders, measured at RT. $SmCo_5$ exhibits typical behavior with milling time, i.e., a sharp increase of H_C for short milling times, a maximum in H_C ($\mu_0 H_C = 1.1$ T after 4 h of milling), followed by a gradual decrease of H_C for long milling times.[12,13] Although

[a)]Electronic mail: dolors.baro@uab.es

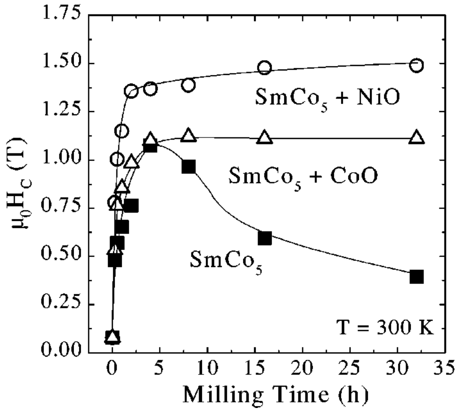

FIG. 1. Milling time dependence of the coercivity, $\mu_0 H_C$ (measured at room temperature) for ball-milled $SmCo_5$ (■), $SmCo_5$–CoO 1:1 (△) and $SmCo_5$–NiO 1:1 (○) powders. The lines are a guide to the eye.

the behavior of the three systems is similar for short milling times, a maximum value of H_C is obtained for $SmCo_5$+NiO, $\mu_0 H_C = 1.5\,\mathrm{T}$. Moreover, in contrast to what is observed for $SmCo_5$ alone, the H_C for $SmCo_5$+NiO and $SmCo_5$+CoO levels off for long milling times. It is also worth noting that even from the early stages of milling an enhancement of H_C is observed in ball-milled $SmCo_5$+NiO in comparison with H_C values of ball-milled $SmCo_5$ and $SmCo_5$+CoO.

As shown in Fig. 2, the coercivities of $SmCo_5$ (milled 4 h) and $SmCo_5$+CoO (milled 32 h) are both found to increase at low temperatures. Note that milling times exhibiting maximum RT H_C were chosen for each system for the field cooling experiments. However, although the RT H_C of both systems is similar, the low temperature coercivity increases further in the $SmCo_5$+CoO system after field cooling ($\mu_0 H_{FC} = 5\,\mathrm{T}$) to below T_N than in $SmCo_5$ alone. Moreover, if $SmCo_5$+CoO is ZFC to low temperatures, the coercivity obtained ($\mu_0 H_C = 2.02\,\mathrm{T}$ at $T = 100\,\mathrm{K}$) is clearly smaller than the one after field cooling ($\mu_0 H_C = 2.19\,\mathrm{T}$ at $T = 100\,\mathrm{K}$). Heat treatments above the T_N of NiO and subsequent field cooling to RT were also carried out for the $SmCo_5$+NiO. However, they resulted in a significant reduction of H_C. Note that small shifts, H_E, of the hysteresis loops in the field axis were often observed for both $SmCo_5$ and $SmCo_5$+CoO ($\mu_0 H_E \sim 0.05\,\mathrm{T}$ at RT and $\mu_0 H_E \sim 0.1\,\mathrm{T}$ at $T = 100\,\mathrm{K}$).

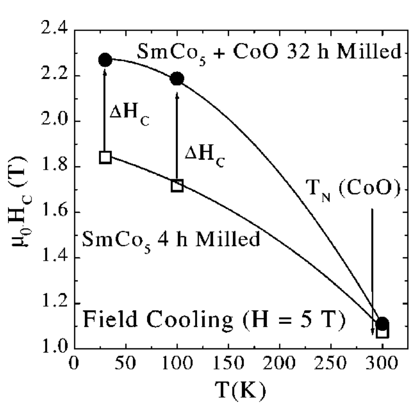

FIG. 2. Temperature dependence of the coercivity, $\mu_0 H_C$, for $SmCo_5$ ball milled for 4 h (□) and $SmCo_5$–CoO 1:1 ball-milled for 32 h (●), after field cooling ($\mu_0 H_{FC} = 5$ T) the as-milled powders to 100 and 30 K. Also indicated is the Néel temperature of CoO ($T_N = 290$ K). The lines are a guide to the eye.

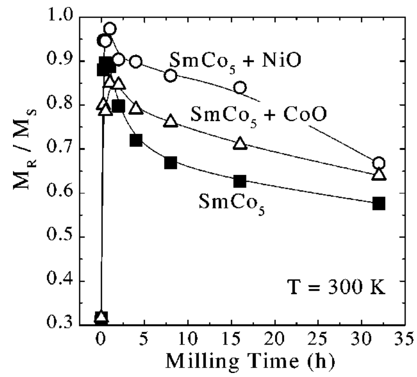

FIG. 3. Milling time dependence of the squareness, M_R/M_S (measured at room temperature) for ball-milled $SmCo_5$ (■), $SmCo_5$–CoO 1:1 (△) and $SmCo_5$–NiO 1:1 (○) powders. The lines are a guide to the eye.

The milling time dependence of the squareness, M_R/M_S, is shown in Fig. 3 for the three systems. It can be seen in Fig. 3 that the squareness of the three systems increases sharply for short milling times. However, the largest M_R/M_S ratio is obtained for $SmCo_5$+NiO, with $M_R/M_S = 0.98$ after 1 h of milling. It should also be noted that M_R/M_S for $SmCo_5$+NiO remains high (>0.85) even for moderate milling times.

The behavior of ball-milled $SmCo_5$ alone has been studied extensively.[12,13] For example, the decrease of H_C observed in $SmCo_5$ for long milling times is known to be due to the tendency towards amorphization of $SmCo_5$ induced by the large amounts of defects introduced after long milling times.[13] As evidenced by XRD results, milling is less aggressive to $SmCo_5$ when it is milled together with CoO or NiO. This could explain why H_C remains large for $SmCo_5$+NiO and $SmCo_5$+CoO even for long milling times. However, although the microstructure and morphology of $SmCo_5$+NiO and $SmCo_5$+CoO are rather similar, the former exhibits a much larger H_C, (Fig. 1). Since NiO is antiferromagnetic at RT ($T_N = 590\,\mathrm{K}$) while CoO is paramagnetic ($T_N = 290\,\mathrm{K}$), this allows the separation of morphological–structural effects from magnetic coupling ones. Thus, the enhanced H_C should be attributed to the existence of FM–AFM exchange coupling in the $SmCo_5$+NiO as-milled powders. Usually, to induce such coupling, a field cooling process through T_N is required.[4] In our case, exchange interactions between the FM and the AFM grains are introduced during milling, without the need of heat treatments. This can be understood because in a planetary mill the temperature can be locally increased in excess of 600 K, due to impacts between the powder and balls.[14] The local field created by the $SmCo_5$ particles plays the role of cooling field during ball–particle impact and induces AFM–FM exchange coupling. Note that it has been demonstrated in thin films that it is the FM moment at the interface rather than the cooling field that controls AFM–FM interface coupling.[15] Since T_N in CoO is lower than RT, no coupling is induced during milling in $SmCo_5$+CoO, thus the RT H_C remains similar to the maximum H_C for ball-milled $SmCo_5$ alone ($\mu_0 H_C = 1.1\,\mathrm{T}$).

However, as shown in Fig. 2, when $SmCo_5$+CoO is field cooled to low temperatures H_C increases substantially. Part of this increase is due to the changes in magnetocrystalline anisotropy of $SmCo_5$, since a similar increase in H_C is observed for $SmCo_5$ alone. Nevertheless, as expected from the FM–AFM coupling, $SmCo_5$+CoO exhibits extra H_C enhancement at low temperatures with respect to single $SmCo_5$ after the same field cooling procedure. Further proof of the effect of FM–AFM coupling comes from H_C in $SmCo_5$+CoO after ZFC. Although the local field of the $SmCo_5$ particles can induce AFM–FM coupling to the CoO even after ZFC from a demagnetized state, only those $SmCo_5$ particles which are single domain will fully contribute to it. In a field cooling experiment ($\mu_0 H_{FC}=5$ T) the total magnetic moment of nearly all $SmCo_5$ particle spins is aligned parallel to the applied field direction, thus all particles contribute to the coupling. Hence, one would expect smaller coupling and consequently reduced H_C enhancement after ZFC, as is observed experimentally.

Unfortunately, field cooling $SmCo_5$+NiO from above T_N of NiO does not result in enhancement of H_C as would be expected from AFM–FM coupling. This is because of the rapid decrease of H_C of $SmCo_5$ when submitted to moderate annealing temperatures, due to the segregation of softer phases (Sm_2Co_7 and Sm_2Co_{17}).[12,16] In other words, the decrease of H_C at $T=600$ K (before the field cooling procedure) is more important than the possible gain due AFM–FM coupling. Note that the local temperature reached during milling can be above the temperature at which soft phases segregate. Nevertheless, the duration of local heating (only effective for a few μs) is exceedingly short to allow diffusion to induce segregation. Hence, the negative effects of the temperature are not observed during milling.

The existence of loop shifts is usually linked to AFM–FM exchange coupling, which strengthens our argument. However, loop shifts have also been observed in $SmCo_5$ alone, which is usually related to interface spin-glass states due to milling induced surface disorder.[13]

Although the Stoner–Wolfarth model[17] for isotropic, single domain, noninteracting particles predicts a squareness of $M_R/M_S=0.5$, small particle hard magnets are known to usually exhibit rather large squareness,[18,19] $M_R/M_S\sim0.8$, similar to the values for $SmCo_5$ shown in Fig. 3. These high M_R/M_S values are due to short-range exchange interactions among $SmCo_5$ particles.[20] Thus, isolating the $SmCo_5$ particles should result in a reduction of M_R/M_S, as observed for $SmCo_5$+CoO after short milling times. Since CoO is paramagnetic at RT, essentially its role is simply to separate the $SmCo_5$ particles. The crossover at moderate milling times between the M_R/M_S of $SmCo_5$+CoO and $SmCo_5$ alone is probably due to the more aggressive effects of milling on $SmCo_5$ alone. Contrary to what is observed in ball-milled $SmCo_5$+CoO, in $SmCo_5$+NiO, even higher M_R/M_S values are obtained in comparison with ball-milled $SmCo_5$. Hence, the presence of the AFM NiO phase surrounding $SmCo_5$ seems to play an important role in further enhancing M_R/M_S. Despite the fact that M_R/M_S enhancement has also been observed in other AFM–FM systems,[10,21] its origin, although clearly related to AFM–FM interaction, is not well understood.

Finally, note that, although the effects described appear to be clearly linked to AFM–FM exchange interactions, some effects from the differences in microstructure and surface disorder cannot be completely ruled out.

In conclusion, we have shown that the coercivity and squareness of permanent magnet powders (e.g., $SmCo_5$) can be enhanced after milling them with an antiferromagnet. To obtain these enhancements at RT and above it is necessary to induce exchange coupling between the permanent magnet and an antiferromagnet with $T_N>$RT. Hence, this study opens up new possibilities for improvement of permanent magnet's magnetic properties.

The authors wish to thank L. Luterotti for his help with the Rietveld fitting. Two of the authors (J.S. and J.N.) thank the DGU and the Spanish government, respectively, for financial support. Partial financial support from CICYT (MAT98-0730), DGR (1999SGR00340) and the Human Potential Program (Contract No. HPRI-1999-CT00030) is also acknowledged.

[1] R. Skomski and J. M. D. Coey, *Permanent Magnetism* (IOP, Bristol, 1999).
[2] G. C. Hadjipanayis, J. Magn. Magn. Mater. **200**, 373 (1999).
[3] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956).
[4] For a recent review, see for example, J. Nogués and I. K. Schuller, J. Magn. Magn. Mater. **192**, 203 (1999).
[5] J. C. S. Kools, IEEE Trans. Magn. **32**, 3165 (1996).
[6] C. Leighton, J. Nogués, B. J. Jönsson-Åkerman, and I. K. Schuller, Phys. Rev. Lett. **84**, 3466 (2000); A. S. Edelstein, R. H. Kodama, M. Miller, V. Browning, P. Lubitz, S. F. Cheng, and H. Sieber, Appl. Phys. Lett. **74**, 3872 (1999); M. D. Stiles and R. D. McMichael, Phys. Rev. B **63**, 064405 (2001).
[7] S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klabunde, J. Appl. Phys. **73**, 6964 (1993).
[8] H. M. Lin, C. M. Hsu, Y. D. Yao, Y. Y. Chen, T. T. Kuan, F. A. Yang, and C. Y. Tung, Nanostruct. Mater. **6**, 977 (1955).
[9] D. S. Geoghegan, P. G. McCormick, and R. Street, Mater. Sci. Forum **179–181**, 629 (1995).
[10] J. Sort, J. Nogués, X. Amils, S. Suriñach, J. S. Muñoz, and M. D. Baró, Appl. Phys. Lett. **75**, 3177 (1999).
[11] $SmCo_5$ powders obtained from Alfa-Aesar®.
[12] For reviews, see, for example, K. J. Strnat and R. M. W. Strnat, J. Magn. Magn. Mater. **100**, 38 (1991); K. Kumar, J. Appl. Phys. **63**, R13 (1988).
[13] D. L. Leslie-Pelecky, E. M. Kirkpatrick, and R. L. Schalek, Nanostruct. Mater. **12**, 887 (1999); D. L. Leslie-Pelecky and R. L. Schalek, Phys. Rev. B **59**, 457 (1999).
[14] P. J. Miller, C. S. Coffey, and V. F. Devost, J. Appl. Phys. **59**, 913 (1986).
[15] P. Miltényi, M. Gierlings, M. Bamming, U. May, G. Güntherodt, J. Nogués, M. Gruyters, C. Leighton, and I. K. Schuller, Appl. Phys. Lett. **75**, 2304 (1999).
[16] K. M. Chowdary, A. K. Giri, K. Pellerin, S. A. Majetich, and J. H. J. Scott, J. Appl. Phys. **85**, 4331 (1999).
[17] E. C. Stoner and E. P. Wohlfarth, Philos. Trans. R. Soc. London, Ser. A **240**, 599 (1948).
[18] R. Coehoorn, D. B. de Mooij, and C. de Waard, J. Magn. Magn. Mater. **80**, 101 (1989).
[19] P. J. McGuiness and S. Kobe, J. Alloys Compd. **281**, 23 (1998); J. Wecker, M. Katter, and L. Schultz, J. Appl. Phys. **69**, 6058 (1991).
[20] T. Schrefl, J. Filder, and H. Kronmüller, Phys. Rev. B **49**, 6100 (1994); A. Hernando, I. Navarro, and J. M. González, Europhys. Lett. **20**, 175 (1992).
[21] B. Gustard and W. J. Schuele, J. Appl. Phys. **37**, 1168 (1966).