

Article VI

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

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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 materials¹ 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 $\text{Nd}_2\text{Fe}_{14}\text{B}$) 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 $\mu_0 H_{\text{max}}=23$ T, by means of an extraction magnetometer. Hysteresis loops after zero-field cooling (ZFC) and field cooling ($\mu_0 H_{\text{FC}}=5$ 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

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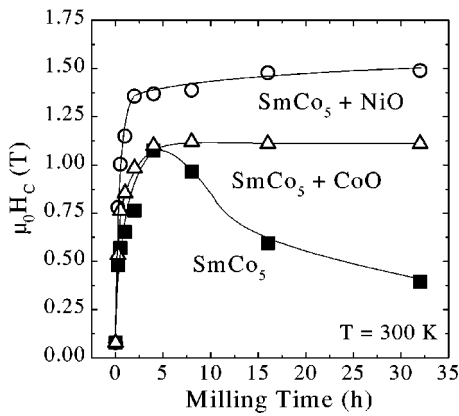


FIG. 1. Milling time dependence of the coercivity, $\mu_0 H_C$ (measured at room temperature) for ball-milled SmCo_5 (■), $\text{SmCo}_5\text{-CoO}$ 1:1 (Δ) and $\text{SmCo}_5\text{-NiO}$ 1:1 (\circ) powders. The lines are a guide to the eye.

the behavior of the three systems is similar for short milling times, a maximum value of H_C is obtained for $\text{SmCo}_5 + \text{NiO}$, $\mu_0 H_C = 1.5 \text{ T}$. Moreover, in contrast to what is observed for SmCo_5 alone, the H_C for $\text{SmCo}_5 + \text{NiO}$ and $\text{SmCo}_5 + \text{CoO}$ 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 $\text{SmCo}_5 + \text{NiO}$ in comparison with H_C values of ball-milled SmCo_5 and $\text{SmCo}_5 + \text{CoO}$.

As shown in Fig. 2, the coercivities of SmCo_5 (milled 4 h) and $\text{SmCo}_5 + \text{CoO}$ (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 $\text{SmCo}_5 + \text{CoO}$ system after field cooling ($\mu_0 H_{FC} = 5 \text{ T}$) to below T_N than in SmCo_5 alone. Moreover, if $\text{SmCo}_5 + \text{CoO}$ is ZFC to low temperatures, the coercivity obtained ($\mu_0 H_C = 2.02 \text{ T}$ at $T = 100 \text{ K}$) is clearly smaller than the one after field cooling ($\mu_0 H_C = 2.19 \text{ T}$ at $T = 100 \text{ K}$). Heat treatments above the T_N of NiO and subsequent field cooling to RT were also carried out for the $\text{SmCo}_5 + \text{NiO}$. 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 $\text{SmCo}_5 + \text{CoO}$ ($\mu_0 H_E \sim 0.05 \text{ T}$ at RT and $\mu_0 H_E \sim 0.1 \text{ T}$ at $T = 100 \text{ K}$).

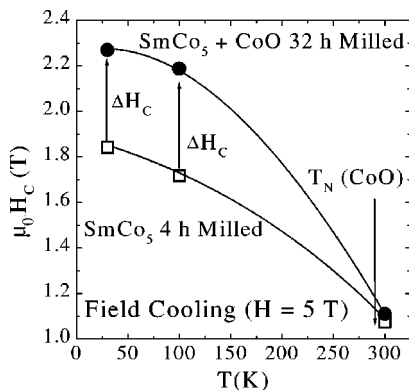


FIG. 2. Temperature dependence of the coercivity, $\mu_0 H_C$, for SmCo_5 ball milled for 4 h (\square) and $\text{SmCo}_5\text{-CoO}$ 1:1 ball-milled for 32 h (\bullet), after field cooling ($\mu_0 H_{FC} = 5 \text{ T}$) the as-milled powders to 100 and 30 K. Also indicated is the Néel temperature of CoO ($T_N = 290 \text{ K}$). The lines are a guide to the eye.

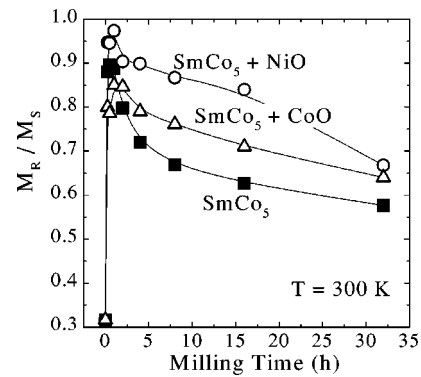


FIG. 3. Milling time dependence of the squareness, M_R / M_S (measured at room temperature) for ball-milled SmCo_5 (■), $\text{SmCo}_5\text{-CoO}$ 1:1 (Δ) and $\text{SmCo}_5\text{-NiO}$ 1:1 (\circ) powders. The lines are a guide to the eye.

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 $\text{SmCo}_5 + \text{NiO}$, with $M_R / M_S = 0.98$ after 1 h of milling. It should also be noted that M_R / M_S for $\text{SmCo}_5 + \text{NiO}$ 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 $\text{SmCo}_5 + \text{NiO}$ and $\text{SmCo}_5 + \text{CoO}$ even for long milling times. However, although the microstructure and morphology of $\text{SmCo}_5 + \text{NiO}$ and $\text{SmCo}_5 + \text{CoO}$ are rather similar, the former exhibits a much larger H_C , (Fig. 1). Since NiO is antiferromagnetic at RT ($T_N = 590 \text{ K}$) while CoO is paramagnetic ($T_N = 290 \text{ K}$), 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 $\text{SmCo}_5 + \text{NiO}$ 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 $\text{SmCo}_5 + \text{CoO}$, thus the RT H_C remains similar to the maximum H_C for ball-milled SmCo_5 alone ($\mu_0 H_C = 1.1 \text{ T}$).

However, as shown in Fig. 2, when $\text{SmCo}_5 + \text{CoO}$ 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 in SmCo_5 alone. The remaining part is due to the induced FM-AFM exchange coupling between the SmCo_5 and CoO grains. This is supported by the fact that the coercivity of $\text{SmCo}_5 + \text{CoO}$ after field cooling is higher than that of SmCo_5 alone. The field cooling process is indicated as $H = 5 \text{ T}$ in Fig. 2.

served 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 $\text{Sm}_2\text{Co}_{17}$).^{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 model¹⁷ 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} $M_R/M_S\sim 0.8$, 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 $T_N>\text{RT}$. Hence, this study opens up new possibilities for improvement of permanent magnet's magnetic properties.

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¹R. Skomski and J. M. D. Coey, *Permanent Magnetism* (IOP, Bristol, 1999).

²G. C. Hadjipanayis, *J. Magn. Magn. Mater.* **200**, 373 (1999).

³W. H. Meiklejohn and C. P. Bean, *Phys. Rev.* **102**, 1413 (1956).

⁴For a recent review, see for example, J. Nogués and I. K. Schuller, *J. Magn. Magn. Mater.* **192**, 203 (1999).

⁵J. C. S. Kools, *IEEE Trans. Magn.* **32**, 3165 (1996).

⁶C. Leighton, J. Nogués, B. J. Jönsson-Akerman, 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).

⁷S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klambunde, *J. Appl. Phys.* **73**, 6964 (1993).

⁸H. 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 (1995).

⁹D. S. Geoghegan, P. G. McCormick, and R. Street, *Mater. Sci. Forum* **179–181**, 629 (1995).

¹⁰J. 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®.

¹²For 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).

¹³D. 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).

¹⁴P. J. Miller, C. S. Coffey, and V. F. Devost, *J. Appl. Phys.* **59**, 913 (1986).

¹⁵P. 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).

¹⁶K. M. Chowdhury, A. K. Giri, K. Pellerin, S. A. Majetich, and J. H. J. Scott, *J. Appl. Phys.* **85**, 4331 (1999).

¹⁷E. C. Stoner and E. P. Wohlfarth, *Philos. Trans. R. Soc. London, Ser. A* **240**, 599 (1948).

¹⁸R. Coehoorn, D. B. de Mooij, and C. de Waard, *J. Magn. Magn. Mater.* **80**, 101 (1989).

¹⁹P. J. McGuinness and S. Kobe, *J. Alloys Compd.* **281**, 23 (1998); J. Wecker, M. Katter, and L. Schultz, *J. Appl. Phys.* **69**, 6058 (1991).

²⁰T. 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).

²¹B. Gustard and W. J. Schuele, *J. Appl. Phys.* **37**, 1168 (1966).

Article VII

Structural and Magnetic Characterization of High-Coercive Ball-Milled Hard Magnetic (SmCo_5) + Antiferromagnetic (NiO) Composites

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Keywords: Ball-Milling, Coercivity, Exchange Bias, Exchange Interactions, Squareness

Abstract Ball-milling induces high values of microstrain and a rapid decrease of the crystallite size in SmCo_5 powders. However, milling is found to be less aggressive to SmCo_5 when it is milled together with a ceramic antiferromagnet, such as NiO. In addition, as the milling proceeds, SmCo_5 particles are progressively surrounded and soldered to NiO, finally becoming embedded in an antiferromagnetic matrix. This microstructure, along with the local heating during the milling, favors the existence of antiferromagnetic-ferromagnetic exchange interactions, which result in an enhancement of the room-temperature coercivity, H_C . Moreover, values of squareness ratio, M_R/M_S (remanence/saturation magnetizations), very close to 1 are found in SmCo_5 +NiO ball-milled for 1 h, without need of particle alignment previously to measurement. The cooperative effects of ferromagnetic-ferromagnetic and antiferromagnetic-ferromagnetic exchange interactions can account for this latter effect.

Introduction

Since its first application to obtain oxide dispersion strengthened (ODS) Ni-based superalloys in 1966 [1], mechanical alloying has become a successful route for the synthesis of a large variety of equilibrium and non-equilibrium phases and phase mixtures [2]. During the last decade, mechanical alloying has also been used for specific purposes, such as the production of materials with giant magnetoresistive properties [3], superconductors [4], materials for hydrogen storage [5] or permanent magnets [6]. Ball-milling can also induce magnetic exchange interactions between soft and hard magnetic materials, leading to a magnetic hardening of the composites [7].

Moreover, intensive research is now being carried out on the effects of exchange interactions between ferromagnetic (FM) and antiferromagnetic (AFM) materials (specially in thin-film form) induced when field cooling the couples through the Néel temperature, T_N , of the AFM [8]. Among them, the shift of the hysteresis loops, commonly known as exchange bias, is the most studied. However, another interesting feature of FM-AFM coupling is the enhancement of the coercivity, H_C . Nevertheless, this effect is seldom studied systematically, especially in small particles. This is in part because in most powder systems this H_C enhancement can only be observed far below room-temperature, either because the AFMs have T_N below room-temperature or their crystallites are so small that they behave superparamagnetically at room-temperature [9,10]. However it has been recently demonstrated that by means of ball-milling of FM with AFM powders (with T_N higher than room-temperature) increases of H_C can be achieved at room-temperature and above [11]. Unfortunately, up to date, this enhancement has only been obtained in soft materials, such as Fe, Ni or Co [11,12]. The purpose of this article is to report the room-temperature coercivity enhancement in SmCo_5 (permanent magnet) ball-milled with NiO and to correlate its structural and magnetic properties.

Experimental

Powders of SmCo_5 (99%, $< 500 \mu\text{m}$, $T_C = 1020 \text{ K}$) [13] were milled alone or together with NiO (99%, $< 44 \mu\text{m}$, $T_N = 590 \text{ K}$) in a weight ratio of 1:1. The milling was carried out for different times

(0.25 - 32 h), using a planetary mill, at 500 rpm, in agate vials ($V = 20$ ml) and 6 agate balls ($\Phi = 10$ mm), with a ball to powder weight ratio of 2:1. The vials were previously sealed under argon atmosphere to prevent oxidation.

The microstructure of the as-milled powders was studied by X-ray diffraction (XRD) ($\text{Cu-K}\alpha$ radiation). The milling time dependences of the crystallite size, $\langle D \rangle$, and microstrain, $\langle \epsilon^2 \rangle^{1/2}$, were evaluated for each component using a full pattern fitting procedure (Rietveld method) [14]. Morphological characterization was performed in powders embedded in epoxy resin using scanning electron microscopy (SEM), equipped with energy dispersive x-ray analysis (EDX) for compositional analysis. Magnetic hysteresis loops of tightly packed isotropic as-milled powders were carried out at room-temperature by means of an extraction magnetometer applying a maximum field of $\mu_0 H_{\text{Max}} = 23$ T.

Results and Discussion

Shown in figure 1 are the x-ray diffraction patterns of $\text{SmCo}_5 + \text{NiO}$ ball-milled for 0.25 h, 4 h and 32 h.

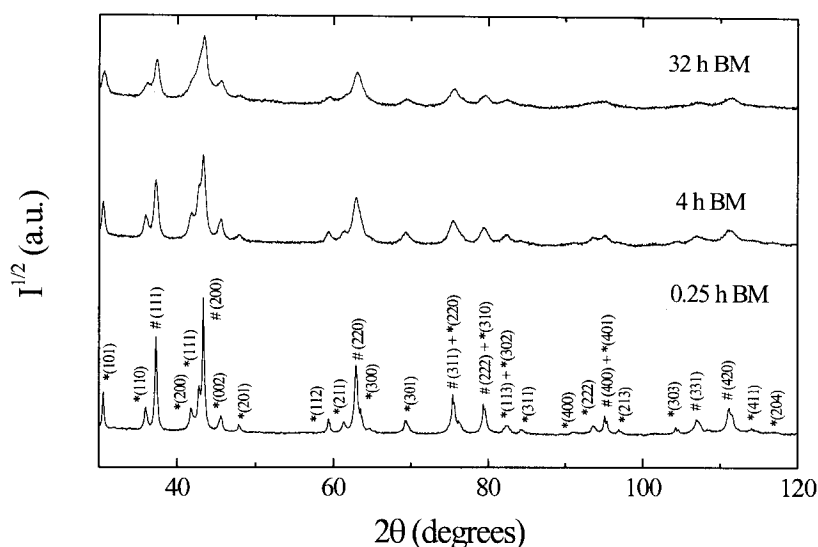


Fig. 1: X-ray diffraction patterns of $\text{SmCo}_5 + \text{NiO}$ ball-milled during 0.25, 4 and 32 h. The symbols * and # denote SmCo_5 and NiO peaks, respectively. Their Miller indexes are also indicated. Note that the diffraction patterns have been shifted for clarity.

The peaks can be indexed to a combination of a hexagonal $P6/mmm$ with cell parameters a and c approximately of 5.005 Å and 3.97 Å (SmCo_5) and a cubic $Fm-3m$ with a approximately equal to 4.1685 Å (NiO) [15]. Note that no peak displacement is observed in figure 1 for different milling times, indicating that the cell parameters remain constant during the milling process, thus implying the lack of atomic interdiffusion between both components. However, the width of the peaks increases for longer milling times, indicating a reduction of the crystallite size and an increase of microstrain. As shown in figure 2, the crystallite size reduction is rather steep for short milling times, although it levels off for longer milling times. It is noteworthy that the crystallite size for SmCo_5 after long-term milling (e.g. 32 h) is much smaller when milled alone ($\langle D \rangle = 2.4$ nm) than when milled with NiO ($\langle D \rangle = 8.9$ nm).

In addition, the microstrain, $\langle e^2 \rangle^{1/2}$, increases with milling time. However, after prolonged millings $\langle e^2 \rangle^{1/2}$ is found to be slightly larger in SmCo_5 than for $\text{SmCo}_5 + \text{NiO}$. Values of $\langle e^2 \rangle^{1/2}$ up to 0.011 are encountered in the 32 h ball-milled SmCo_5 . This is an indication that large amounts of structural defects, such as dislocations or vacancies, are introduced in the material during the milling. The small crystallite size and the large microstrain for SmCo_5 milled alone indicate that after 32 h SmCo_5 is close to amorphization, as already reported by other groups [16,17]. Conversely, the milling appears to be less aggressive when SmCo_5 is milled with NiO.

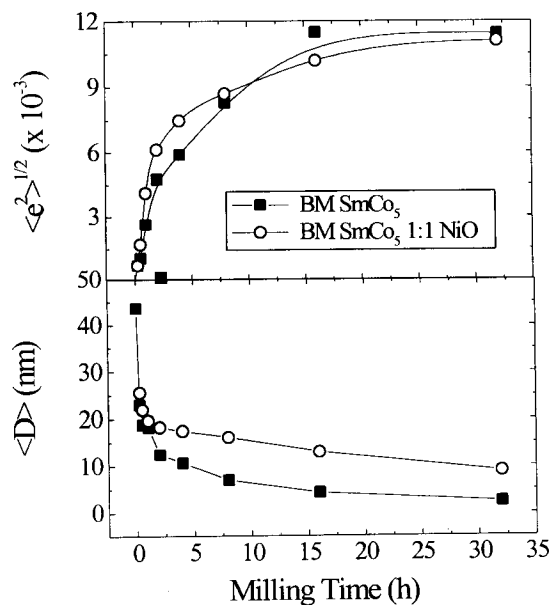


Fig. 2: Milling time dependences of the SmCo_5 microstrain, $\langle e^2 \rangle^{1/2}$ and crystallite size, $\langle D \rangle$, in ball-milled SmCo_5 alone and ball-milled SmCo_5 with NiO (1:1). Note that the lines are a guide to the eye.

From SEM observations (not shown) the starting SmCo_5 particles are irregular-shaped with sizes of up to 500 μm . When ball-milled alone they are progressively fractured and reduced in size, turning into small roughly spherical particles, with sizes ranging from around 1 to 30 μm after 32 h of milling.

However, as can be seen in figure 3 (a) when SmCo_5 powders are ball-milled with NiO a different microstructure is encountered. At the first stages of milling the powders mix and the grain size starts to reduce. As the milling proceeds, the SmCo_5 particles tend to become elongated and embedded in a NiO matrix. This is due to the more ductile character of SmCo_5 , compared to the brittle NiO. These agglomerates start to form after a few hours of milling and grow in size as the milling time is increased. Co, Ni and Sm EDX mappings, shown respectively in figures 3 (b), 3 (c) and 3 (d), confirm that the elongated particles correspond to SmCo_5 , while the matrix is NiO. The black regions in figure 3 (a) are epoxy resin. From these mappings the absence of strong atomic interdiffusion between SmCo_5 and NiO during the milling is confirmed. This microstructure, typical of ball-milled metal-ceramics [18,19], allows the existence of a large amount of interfaces between the FM and the AFM phases.

The milling time dependences of H_C and the squareness ratio, M_R/M_S (where M_R is the remanence magnetization) for ball-milled SmCo_5 alone have been reported by several authors [16,17]. The starting SmCo_5 particles exhibit low values of H_C and M_R/M_S , thus not showing the

typical hard ferromagnetic behavior. This can be mainly attributed to the large size of the particles. The original SmCo_5 particles are, due to their size, in a multi-domain state, hence no hard magnetic character is expected. Moreover, the long-range dipolar interactions, which reduce significantly H_C and M_R/M_S , have higher effects on particles with large sizes [20]. In addition, sharp corners existing in the inhomogeneous SmCo_5 as-obtained particles, give rise to large stray fields, which have a demagnetizing effect, hence also giving rise to low values of H_C . As the milling time increases H_C is gradually increased due to the reduction of the particle size into a single-domain state and the milling-induced smoothness of the particles. H_C exhibits a maximum after 4 h of milling ($\mu_0 H_C = 1.1$ T) and progressively reduces with milling time, reaching $\mu_0 H_C = 0.7$ T after 32 h of milling. The decrease of H_C after long-term milling can be mainly attributed to the amorphization of SmCo_5 particles that progressively reduces their hard magnetic properties [16,17].

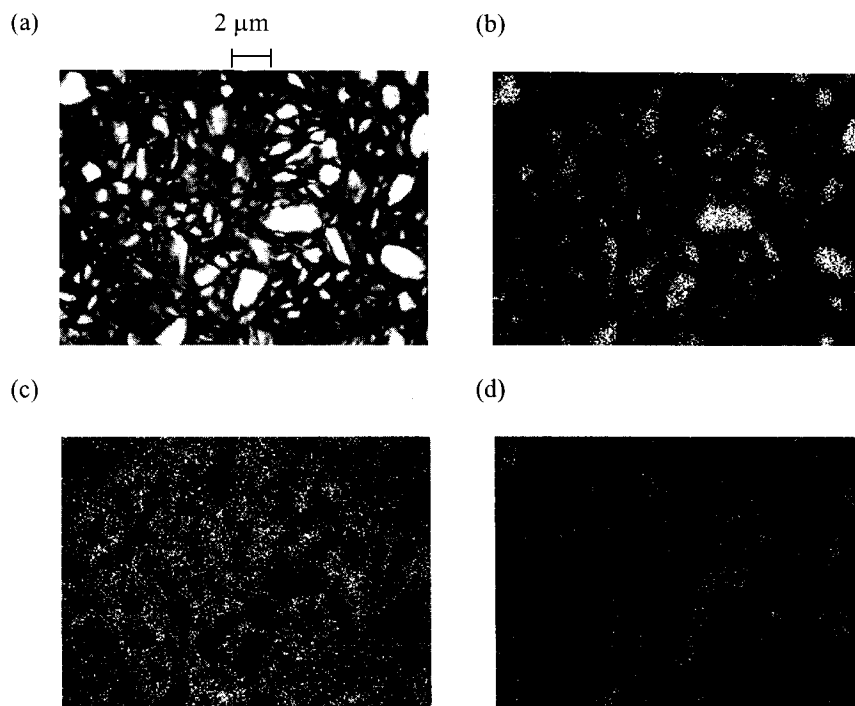


Fig. 3: (a) SEM image (backscattered electrons) with the corresponding Co (b), Ni (c) and Sm (d) EDX mappings for SmCo_5 ball-milled with NiO for 32 h.

However, ball-milling of $\text{SmCo}_5 + \text{NiO}$ develops into a rather different behavior [21]. Although H_C also increases during the first stages of milling ($\mu_0 H_C = 1.37$ T after 4 h), it continues to increase slightly even for longer milling times, up to $\mu_0 H_C = 1.5$ T after 32 h of milling. The difference in coercivity between both systems (SmCo_5 milled for 4 h and $\text{SmCo}_5 + \text{NiO}$ milled for 32 h, i.e. the milling times giving largest H_C in each system) is shown in fig. 4. Note the decrease of the saturation magnetization, M_S , in the latter case is due to the zero M_S of NiO (AFM). The shoulder of the hysteresis loop observed in $\text{SmCo}_5 + \text{NiO}$ ball-milled for 32 h is not likely to be related to the presence of two magnetic phases, since XRD revealed only the hard SmCo_5 magnetic phase. Hence, we attribute this shoulder to the existence of different degrees of coupling between the SmCo_5 and the NiO particles.

The differences in microstructure between SmCo_5 milled alone and milled with NiO (e.g. isolated particles and larger crystallite size in the latter case) are partially responsible for the

observed increase of H_C , especially for long milling times. However, it has been observed in SmCo_5 ball-milled with CoO (paramagnetic at room-temperature, $T_N = 290 \text{ K}$) that, although a completely analogous microstructure to $\text{SmCo}_5 + \text{NiO}$ is developed, the maximum value of H_C is only $\mu_0 H_C = 1.12 \text{ T}$, after 32 h of milling (comparable to the maximum H_C in ball-milled SmCo_5 alone) [21]. Hence, the differences in microstructure in the different cases can only account for part of the observed H_C enhancement. Therefore, it is clear that AFM-FM exchange interactions, introduced during the milling of $\text{SmCo}_5 + \text{NiO}$, can induce a further enhancement of H_C . However usually a field-cooling process through T_N is required to cause such a coupling [8]. In our case, since temperature can be locally raised to more than 600 K during the milling due to the impacts between powder and balls [22] and SmCo_5 particles can create considerable microscopic magnetic fields to the neighbouring NiO particles, it is reasonable to assume that exchange interactions can be created during the milling without need of subsequent heat treatments.

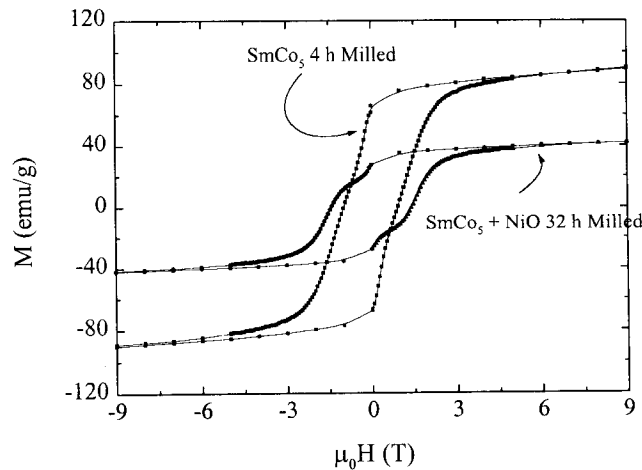


Fig. 4: Enlargements of the hysteresis loops (in the field range -9 to 9 T) of SmCo_5 and $\text{SmCo}_5 + \text{NiO}$ ball-milled for 4 and 32 h, respectively.

Furthermore, a dramatic enhancement of squareness M_R/M_S is observed after short-term milling. Although the Stoner-Wolfarth model for isotropic, single domain and non-interacting particles predicts a squareness of $M_R/M_S = 0.5$ [23], values of M_R/M_S as high as 0.9 are obtained in SmCo_5 milled for 0.5 h [21], without aligning the powders previously to measurement. Remanence enhancement in isotropic FM particles, which has also been observed in other ball-milled hard magnets, such as NdFeB or SmFeN [24], is related to short-range exchange interactions between ferromagnetic grains [25]. As the crystallite size is reduced so abruptly during first stages of milling (see figure 2), each SmCo_5 particle is composed of a large number of crystallites. Usually exchange interactions between grains produce a perturbed region restricted to the crystallite boundary in which, once the field is removed, the spins remain oriented in the previous magnetizing field direction, resulting in the high values of M_R . Somewhat higher values of M_R/M_S are obtained in ball-milled $\text{SmCo}_5 + \text{NiO}$ for all milling times ($M_R/M_S = 0.98$ for $\text{SmCo}_5 + \text{NiO}$ ball-milled for 1h). Although not fully understood, it seems that the interplay between FM-FM and FM-AFM exchange interactions can yield to very high M_R/M_S values.

Conclusions

In conclusion, we have shown that ball-milled hard magnetic (SmCo_5) (1):(1) AFM (NiO) powders exhibit a significant enhancement of the room-temperature coercivity, H_C , and squareness, M_R/M_S ,

as compared to SmCo₅ ball-milled alone. These effects are due, at least in part, to FM-AFM exchange interactions induced by the local heating during the milling. We have shown that NiO also plays an important role in slowing down SmCo₅ structural changes, thus avoiding the amorphization-induced H_c decrease during the milling. It is also interesting that the microstructure developed during the milling process, with a large number of interfaces between the FM and the AFM components, is likely to favor the existence of AFM-FM exchange interactions.

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References

- [1] J.S. Benjamin, Metall. Trans. 1 (1970) p. 2943.
- [2] B.S. Murty, S. Ranganathan, Internat. Mater. Rev. 43 (1998) p. 101.
- [3] K. Yasuna, A. Otsuki, K.N. Ishihara, P.H. Shingu, Mater. Sci. Forum 235-238 (1997) p. 825.
- [4] J. Saida, Y. Tanaka, K. Okazaki, Mater. Trans. JIM 37 (1996) p. 265.
- [5] W. Liu, H. Wu, Y. Lei, Q. Wang, J. Wu, J. Alloys Compd. 252 (1997) p. 234.
- [6] L. Schultz, J. Wecker, E. Hellstern, J. Appl. Phys. 61 (1987) p. 3583; W. F. Miao, J. Ding, P.G. McCormick, R. Street, J. Appl. Phys. 79 (1996) p. 2079.
- [7] K. Raviprasad, M. Funakoshi, M. Umemoto, J. Appl. Phys. 83 (1998) p. 921.
- [8] For recent reviews see: J. Nogués and I. K. Schuller, J. Magn. Magn. Mater. 192 (1999) p. 203; A.E. Berkowitz and K. Takano, J. Magn. Magn. Mater. 200 (1999) p. 552; R.L. Stamps, J. Phys. D: Appl. Phys. 33 (2000) p. R247.
- [9] H.M. Lin, C.M. Hsu, Y.D. Yao, Y.Y. Chen, T.T. Kuan, F.A. Yang, C.Y. Tung, Nanostruct. Mater. 6 (1995) p. 977.
- [10] S. Gangopadhyay, G.C. Hadjipanayis, C.M. Sorensen, K.J. Klabunde, J. Appl. Phys. 73 (1993) p. 6964.
- [11] J. Sort, J. Nogués, X. Amils, S. Suriñach, J.S. Muñoz, M.D. Baró, Appl. Phys. Lett. 75 (1999) p. 3177.
- [12] D.S. Geoghegan, P.G. McCormick, R. Street, Mater. Sci. Forum 179-181 (1995) p. 629.
- [13] Alfa-Aesar®.
- [14] L. Lutterotti, S. Gialanella, Acta Mater. 46 (1997) p. 101.
- [15] P. Villars, L.D. Calvert: *Person's Handbook of Crystallographic Data for Intermetallic Phases*, (American Society for Metals, United States 1986).
- [16] For reviews see: K. J. Strnat and R. M. W. Strnat, J. Magn. Magn. Mater. 100 (1991) p. 38; K. Kumar, J. Appl. Phys. 63 (1988) p. R13.
- [17] D. L. Leslie- Pelecky, E. M. Kirkpatrick, and R. L. Schalek, Nanostruct. Mater. 12 (1999) p. 887; D. L. Leslie-Pelecky and R. L. Schalek, Phys. Rev. B 59 (1999) p. 457.
- [18] T. Klassen, G. Günther, B. Dickau, A. Bartels, R. Bormann, H. Mecking, Mater. Sci. Forum 269-272 (1998) p. 37.
- [19] J. Sort, J. Nogués, X. Amils, S. Suriñach, J.S. Muñoz, M.D. Baró, Mater. Sci. Forum, 343-346 (2000) p. 812.
- [20] T. Schrefl, H.F. Schmidts, J. Fidler, H. Kronmüller, J. Magn. Magn. Mater. 124 (1993) p. 251; W. Rave, K. Ramstöck, J. Magn. Magn. Mater. 171 (1997) p. 69.
- [21] J. Sort, J. Nogués, S. Suriñach, J. S. Muñoz, E. Chappel, F. Dupont, G. Chouteau, M. D. Baró, Appl. Phys. Lett. (2001) in press.
- [22] P.J. Miller, C.S. Coffey, V.F. Devost, J. Appl. Phys. 59 (1986) p. 913.
- [23] E. C. Stoner and E. P. Wohlfarth, Philos. Trans. R. Soc. 240 (1948) p. 599.

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- [24] P. J. McGuinness and S. Kobe, *J. Alloys and Compounds* 281 (1998) p. 23; J. Wecker, M. Katter, and L. Schultz, *J. Appl. Phys.* 69 (1991) p. 6058.
- [25] T. Schrefl, J. Fidler, and H. Kronmüller, *Phys. Rev. B* 49 (1994) p. 6100; A. Hernando, I. Navarro, and J. M. González, *Europhys. Lett.* 20 (1992) p. 175.

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