

Article VIII

Improving the energy product of hard magnetic materials

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A route toward enhancing the energy product $(BH)_{\max}$ of permanent magnetic materials, at room temperature, based on ferromagnetic-(FM-) antiferromagnetic (AFM) exchange interactions has been developed. The exchange coupling, which is induced by ball milling hard magnetic SmCo_5 with AFM NiO powders, results in an enhancement of coercivity H_C and squareness ratio M_R/M_S (remnant-saturation magnetizations), which depends on the FM:AFM ratio and the processing conditions. However, the presence of the AFM in the composite results also in a competing effect, i.e., reduction of the overall saturation magnetization, which decreases $(BH)_{\max}$. Nevertheless, it has been found that after an optimization of the FM:AFM ratio and the milling conditions it is possible to achieve an improvement of $(BH)_{\max}$.

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During the last few decades the improvement of the permanent magnet quality has been mainly centered on the development of materials with high magnetic anisotropies, such as SmCo_5 or NdFeB .^{1,2} However, due, in part, to the difficulty of finding ferromagnetic materials with ever-increasing magnetocrystalline anisotropies, a class of permanent magnets, based on the exchange interactions between hard and soft magnetic phases, has been proposed.³⁻⁵ In these composites, usually denoted as spring magnets, the ferromagnetic exchange interactions result in an increase of the remanent and saturation magnetizations M_R and M_S as well as their ratio M_R/M_S . However, the presence of a soft phase usually induces a decrease of the coercivity H_C when compared to the hard phase alone.⁴ Nevertheless, despite the H_C reduction, the energy product of the composites can be enhanced when their microstructure is optimized.⁵

In this framework, we have recently demonstrated that a significant H_C enhancement in hard magnetic materials can be achieved by means of exchange interactions between ferromagnetic (FM) and antiferromagnetic (AFM) phases (exchange bias).⁶ Exchange bias, which typically results in a shift and a widening of the hysteresis loop, has been extensively studied, especially in thin films, because of the role of the loop shift in spin-valve devices.⁷ However, despite its potential technological interest, H_C enhancement has been much less studied.⁸ In this paper we exploit this latter effect in powder systems to demonstrate that, under suitable conditions, AFM-FM coupling can not only lead to H_C enhancements, but also to the improvement of the figure of merit of permanent magnet materials, i.e., the energy product $(BH)_{\max}$. However, the reduction of the overall M_S of the composites due to the presence of the AFM phase has to be

taken into account. Thus, similar to spring magnets, AFM-FM exchange interactions also result in two opposite effects. Consequently, tuning of the FM/AFM ratio is necessary to accomplish $(BH)_{\max}$ enhancements at room temperature.

It has been demonstrated that ball milling FM with AFM particles is an effective way to create a large number of FM/AFM interfaces.⁹ However, studies of AFM-FM coupling in mechanically milled materials are scarce.^{10,11} Moreover, in most studies of small particles, the AFM-FM interactions take place only at low temperatures, either because the Néel temperature T_N is below room temperature or the AFM grains are so small that they behave superparamagnetically at room temperature.¹²

In this study we have ball milled hard-FM SmCo_5 (Ref. 13) (99%, -30 mesh) alone and together with NiO (99%, -325 mesh), in the weight ratios of SmCo_5 :NiO 3:1, 3:2, and 1:1. Since T_N (NiO) is about 525 K, the effects of AFM-FM coupling can be achieved at room temperature. The milling has been carried out in a planetary ball mill using agate vials and agate balls, under argon atmosphere, at 500 rpm and with a ball to powder weight ratio of 2:1. The milling time ranges from 0.25 to 32 h. The structural characterization has been performed by x-ray diffraction (XRD), from which the patterns have been fitted using the Rietveld method to determine the crystallite sizes and microstrains.¹⁴ In addition, the morphology and composition developed during the different stages of milling have been analyzed by scanning electron microscopy (SEM), including energy-dispersive x-ray analyses (EDX), in powders embedded in epoxy resin and polished with diamond paste. The magnetic measurements have been performed using an extraction mag-

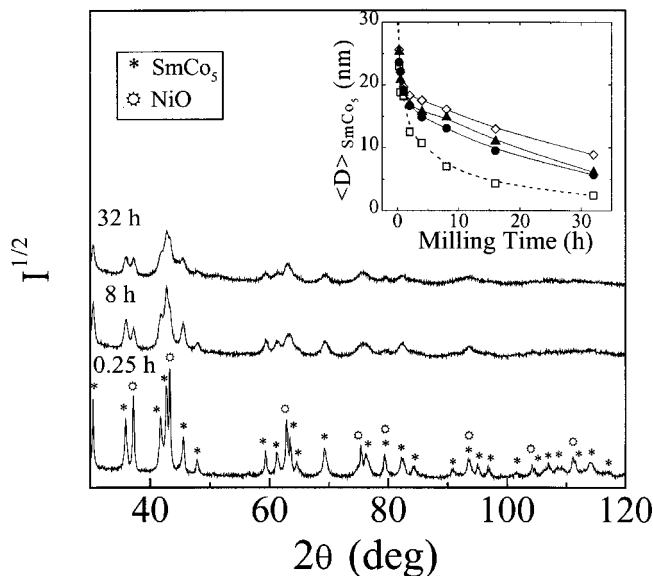


FIG. 1. XRD patterns of SmCo₅ milled with NiO during 0.25, 8, and 32 h in the weight ratio of 3:1. In the inset, milling time dependence of the SmCo₅ crystallite size $\langle D \rangle_{\text{SmCo}_5}$ for the SmCo₅:NiO weight ratios 1:0 (—□—), 3:1 (—●—), 3:2 (—▲—), and 1:1 (—◇—). Note that, for clarity, the crystallite size of the starting SmCo₅ powders (i.e., $\langle D \rangle_{\text{SmCo}_5, \text{initial}} = 43$ nm) has not been plotted. The lines are a guide to the eye.

netometer, with a maximum applied field of $\mu_0 H = 23$ T, in tightly packed isotropic powders. The angular dependence of the magnetization was measured using vector magnetometry in a field of $\mu_0 H = 5$ T, in oriented powders embedded in resin.

Shown in Fig. 1 are the XRD patterns of SmCo₅ milled with NiO in a weight ratio of 3:1, for 0.25, 8, and 32 h. As can be seen in the figure, no extra peaks, apart from those of SmCo₅ and NiO, appear during the milling. Further, the diffraction peaks are not found to shift in angle as the milling proceeds, indicating the absence of significant atomic interdiffusion between both components. However, a remarkable broadening of the peaks is observed, which is mainly attributed to the crystallite size reduction and the microstrain increase during the milling. In the inset, the milling time dependence of SmCo₅ crystallite size $\langle D \rangle_{\text{SmCo}_5}$ is shown for different NiO contents. For all compositions, $\langle D \rangle_{\text{SmCo}_5}$ is found to decrease steeply for short milling times ($\langle D \rangle_{\text{SmCo}_5} = 43$ nm for the starting powders) leveling off at values below 10 nm after long-term milling. In addition, slightly smaller values of the stacking fault probability α are found for increasing NiO content, although they remain relatively small for all compositions, even for long-term milling [e.g., α_{SmCo_5} (32 h) $\sim 3 \times 10^{-3}$, $\alpha_{\text{SmCo}_5 + \text{NiO}}$ (32 h) $\sim 1 \times 10^{-3}$]. Moreover, microstrains, $\langle \epsilon^2 \rangle^{1/2}$, are found to increase with milling time for all compositions. However they remain similar for the different SmCo₅:NiO ratios during the milling (e.g., $\langle \epsilon^2 \rangle^{1/2} \sim 8 \times 10^{-3}$ after milling for 32 h). The small crystallite sizes and large microstrains for long milling times imply severe plastic deformation and hence a high degree of structural disorder.^{2,15} Nevertheless, when SmCo₅ is

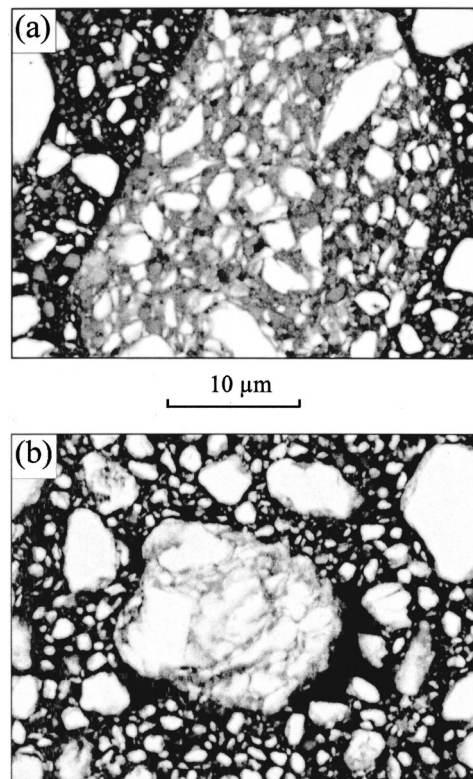


FIG. 2. SEM images (backscattered electrons) of SmCo₅ milled with NiO during 16 h in the weight ratios of (a) 1:1 and (b) 3:1. The bright particles correspond to SmCo₅ while the gray areas to NiO. Note that the black regions are epoxy resin.

milled with NiO, the crystallite size reduction due to the milling becomes smoother. These results clearly show that NiO slows down SmCo₅ crystallite size refinement induced during the milling.⁹

Shown in Fig. 2 are scanning electron microscopy (SEM) images (backscattered electrons) of SmCo₅ milled for 16 h with NiO in the weight ratios 1:1 [Fig. 2(a)] and 3:1 [Fig. 2(b)]. Energy dispersive x-ray analyses (not shown) revealed that the bright particles correspond to SmCo₅, while the gray zones correspond to NiO (the black regions are epoxy resin). The original SmCo₅ particles are found to be rather irregular shaped and to have a broad particle size distribution (from a few μm to more than 200 μm). When they are milled alone they are progressively fractured and reduced in size, turning into small roughly spherical particles, with sizes ranging from 1 to 30 μm after milling for 32 h. However, as can be seen in Fig. 2, a different microstructure develops when SmCo₅ is milled with NiO. After short-term milling the powders mix and the crystallite size is reduced. However, as the milling proceeds, SmCo₅ particles start to solder with NiO and finally become embedded in an AFM matrix. SEM observations reveal that some small clusters are already formed after a few hours of milling, which grow in size as the milling proceeds. These agglomerates are found to develop more easily as the NiO content is increased. Thus, after milling for 16 h the average agglomerate size for the 1:1 ratio is of around 30 μm whereas for SmCo₅(3):(1)NiO agglomerates larger than 15 μm are rarely obtained. Furthermore, the

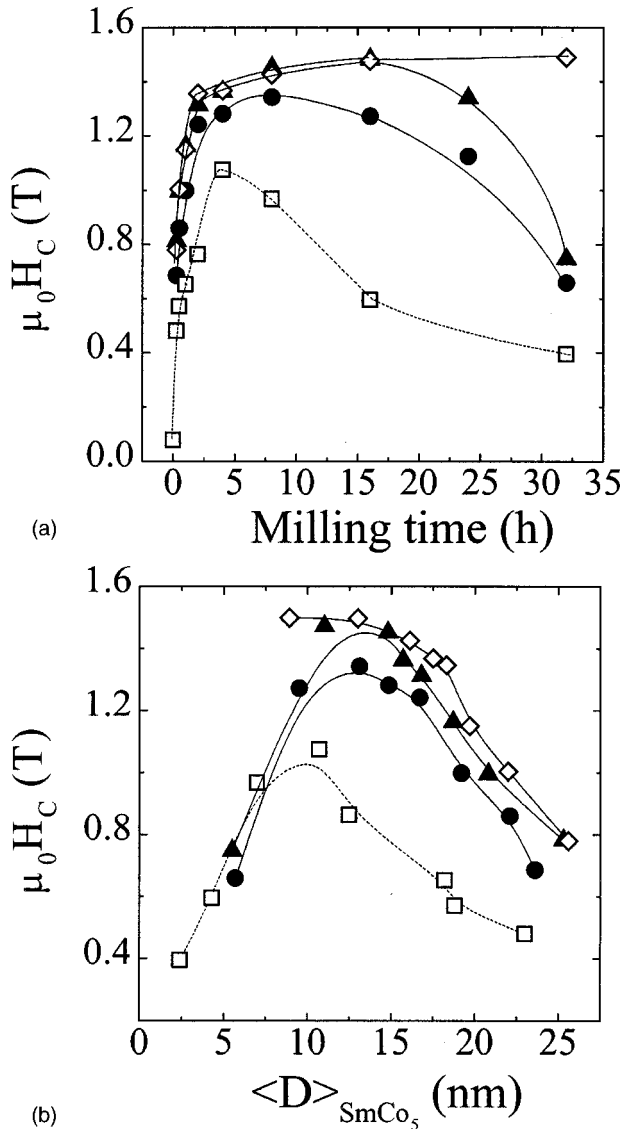


FIG. 3. (a) Milling time dependence of the coercivity $\mu_0 H_C$ for SmCo₅ milled with NiO in the weight ratios 1:0 (—□—), 3:1 (—●—), 3:2 (—▲—), and 1:1 (—◇—). (b) Dependence of $\mu_0 H_C$ on the SmCo₅ crystallite size $\langle D \rangle_{\text{SmCo}_5}$, for SmCo₅ milled with NiO in the same weight ratios. Note that, for clarity, the value of $\mu_0 H_C$ for the starting SmCo₅ powders has not been plotted in Fig. 3(b). Also note that the error bars are smaller than the symbols. The lines are a guide to the eye.

amount of FM in each cluster is clearly larger for the 3:1 ratio. However, in both cases, the large amount of interfaces between SmCo₅ and NiO created in these composites makes this microstructure very favorable for the induction of AFM-FM exchange interactions.

The evolution of the magnetic properties of SmCo₅ when subject to ball milling has been extensively studied.^{2,15} Briefly, as can be seen in Fig. 3(a), $\mu_0 H_C$ is found to increase with milling time, reaching a maximum value of approximately 1.1 T after 4 h and decreases afterwards to about 0.4 T after 32 h. The increase of H_C for short-term milling is attributed to particle size reduction, which converts them from a multidomain to a monodomain state. As shown in

Fig. 3(b) H_C achieves its maximum value for a crystallite size $\langle D \rangle_{\text{SmCo}_5}$, of around 10 nm, in good agreement with other works on ball milled SmCo₅.¹⁵ Nevertheless, when SmCo₅ is overmilled it tends to become highly disordered and its crystallite size is significantly reduced, losing part of its high magnetic anisotropy, thus reducing H_C .^{2,15}

It is noteworthy that, usually, in order to induce AFM-FM coupling a field cooling process through the AFM Néel temperature is required.⁷ However, during the milling, due to the impacts between powders and balls, temperature can be locally raised to above T_N .¹⁶ Moreover, due to their high magnetocrystalline anisotropy, SmCo₅ particles can create considerable microscopic magnetic fields to the neighboring NiO grains. Therefore, effectively, the field cooling process through T_N can actually take place during the milling. This effect is similar to the creation of domains by local flash annealing in AFM/FM bilayers.¹⁷ As shown in Fig. 3(a), when SmCo₅ is milled with NiO a remarkable enhancement of $\mu_0 H_C$ is obtained, e.g., $H_C = 1.5$ T in SmCo₅ (1):(1) NiO milled for 32 h, as expected from the AFM-FM coupling. The existence of the AFM/FM coupling has been demonstrated indirectly.⁶ However, it is difficult to directly show its existence mainly due to the magnetic and structural character of SmCo₅ and NiO. Namely, the magnetocrystalline anisotropy of NiO is exceedingly small to allow for the existence of significant loop shifts when coupled to SmCo₅. Furthermore, SmCo₅ is known to undergo structural transitions when heated,³ even at temperatures below the T_N of NiO, which impede the analysis of the temperature dependence of the coercivity enhancement. Moreover, the random character of the ball milled powders makes it difficult to search for unidirectional anisotropy using torque magnetometry. Nevertheless, if magnetic measurements are carried out on oriented as-milled SmCo₅ + NiO powders, there is evidence from the angular dependence of the magnetization for the presence of a unidirectional component, superimposed to the expected uniaxial component of the anisotropy, indicating the existence of AFM-FM coupling.¹⁸ Moreover, this unidirectional anisotropy component increases as temperature is decreased, as expected from the increase of AFM anisotropy.⁷ In addition, although milling with CoO (paramagnetic at room temperature) results in an analogous microstructure, it has been found that the maximum H_C in this case does not overcome the maximum H_C of SmCo₅ milled alone. At room temperature [i.e., above the $T_N(\text{CoO}) = 290$ K] the role of CoO is to merely separate the SmCo₅ particles, thus reducing the exchange interactions between them. The fact that H_C is larger for SmCo₅ + NiO than for SmCo₅ + CoO for all milling times indicates that the role of NiO (AFM at room temperature) is more than to simply separate the SmCo₅ particles. Moreover, if in the SmCo₅ + CoO system the temperature is reduced to below CoO T_N (~ 290 K) there is a clear enhancement of H_C , which is a further proof of the role of AFM-FM exchange interactions in enhancing H_C .⁶ However, it is important to point out that microstructural effects also play a role, especially in the evolution of the coercivity during the milling.

As can be seen in Fig. 3, for a fixed milling time [Fig. 3(a)] or a fixed crystallite size [Fig. 3(b)], H_C is found to

increase with the NiO content. Moreover, the maximum value of H_C , is observed, for all compositions, for $\langle D \rangle_{\text{SmCo}_5}$ between 10 and 15 nm [see Fig. 3(b)]. Note that it was also found that, for all milling times and crystallite sizes, H_C in $\text{SmCo}_5 + \text{CoO}$ remained always between those of SmCo_5 and $\text{SmCo}_5 + \text{NiO}$.⁶ Moreover, contrary to what has been observed for the crystallite size, $\langle D \rangle_{\text{SmCo}_5}$, no systematic correlation between stacking fault probability and H_C has been found, probably because the stacking fault probability remains relatively small for all compositions, even for long milling times. This again implies that the role of NiO is not simply to change the microstructure of SmCo_5 or isolate the different SmCo_5 grains, but AFM-FM exchange interactions play a key role in the enhancement of H_C . The increase of H_C for increasing NiO contents can be understood in terms of the microstructure developed in the composites. The agglomerates, in which FM and AFM are soldered together, where AFM-FM exchange interactions are more likely to take place, form more easily for higher AFM contents. However, due to the different degrees of SmCo_5 dispersion in the agglomerates for different NiO contents, changes in the FM-FM interactions when changing the composition are also likely to play some role in H_C . Moreover, the milling time at which H_C exhibits its maximum value for each composition shifts towards higher values as the NiO content is increased. This is due to the role of NiO in slowing down the microstructural changes, especially the SmCo_5 crystallite size refinement, which delays the decrease of H_C .

Furthermore, very high values of M_R/M_S , close to 1, have also been obtained in isotropic powders, for all compositions, especially after short-term milling [e.g., after 1 h of milling $M_R/M_S(\text{SmCo}_5) \approx 0.9$, while $M_R/M_S(1:1) \approx 0.98$].⁶ Enhancements of M_R/M_S are not unusual in ball milled hard magnetic materials and are generally attributed to short-range exchange interactions between the different FM grains.¹⁹ However, especially for long milling times, M_R/M_S of FM/AFM composites remain larger than the one for SmCo_5 alone [e.g., after 16 h of milling $M_R/M_S(\text{SmCo}_5) \approx 0.6$, $M_R/M_S(3:1) \approx 0.7$, $M_R/M_S(3:2) \approx 0.75$, and $M_R/M_S(1:1) \approx 0.85$], in agreement with other AFM/FM powder systems,^{11,20} indicating that AFM/FM coupling may play also some role in enhancing M_R/M_S .

The figure of merit in a hard magnetic material is not so much H_C or M_R/M_S but its energy product $(\text{BH})_{\text{max}}$, which gives an idea of the amount of energy that can be stored in the magnet. Thus, the size of a magnet required to create a given magnetic field is roughly inversely proportional to its $(\text{BH})_{\text{max}}$.¹ The energy product of a magnet can be improved if its H_C , M_S , or M_R/M_S are increased, since it depends on the total area enclosed by the hysteresis loop. In Fig. 4, the milling time dependence of $(\text{BH})_{\text{max}}$ is shown for different AFM:FM ratios. It can be observed that the dependence of $(\text{BH})_{\text{max}}$ on the AFM content is rather complex. This is because of the opposing effects of the AFM in the enhancement of $(\text{BH})_{\text{max}}$. On the one hand, both H_C and M_R/M_S increase

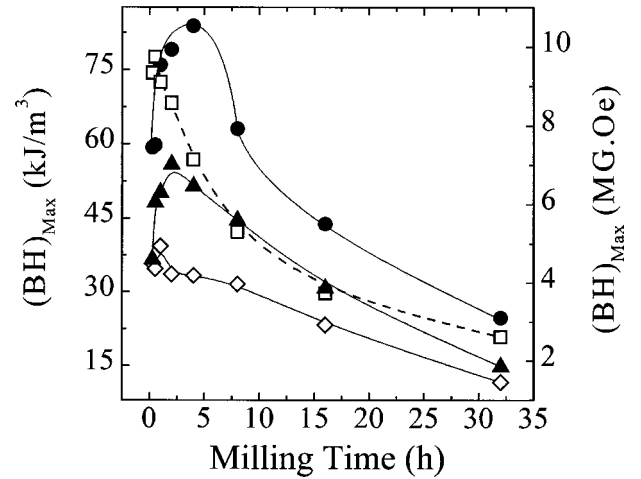


FIG. 4. Milling time dependence of the energy product $(\text{BH})_{\text{max}}$, for SmCo_5 milled with NiO in the weight ratios 1:0 (---□---), 3:1 (—●—), 3:2 (—▲—), and 1:1 (—◇—). Given on the right axis are the $(\text{BH})_{\text{max}}$ values in cgs units. Note that the error bars are smaller than the symbols. The lines are a guide to the eye.

due to the FM-AFM and FM-FM exchange interactions. On the other hand, the presence of NiO results in a reduction of the saturation magnetization of the composite, proportional to the NiO content. This stems from the zero net magnetization of the AFM ($M_{\text{AFM}}=0$), which does not contribute to the overall saturation magnetization. Consequently, as seen in Fig. 4, $(\text{BH})_{\text{max}}$ is reduced when the NiO content is increasingly high, as, for example, in the case of the 1:1 ratio. Nevertheless, $(\text{BH})_{\text{max}}$ for the SmCo_5 (3):(1) NiO milled for 4 h exhibits an enhancement with respect to the maximum of pure SmCo_5 . Therefore, due to the interplay of all the different effects, an enhancement of $(\text{BH})_{\text{max}}$ can only be achieved through the optimization of the FM: AFM ratio and processing conditions.

In conclusion, we have shown that by ball milling a hard magnetic material, such as SmCo_5 , with AFM NiO powders, in the appropriate FM:AFM ratio, it is possible to enhance the key factor in hard magnetic materials, i.e., the energy product at room temperature. This effect is controlled by the interplay between the coercivity and squareness ratio enhancement, mainly due to the AFM-FM coupling, the M_S reduction due to the $M_{\text{AFM}}=0$ and the microstructure of the composite. Consequently, we believe that this procedure can lead to a new route for the improvement of permanent magnet quality.

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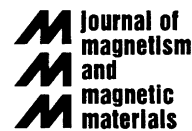
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Article IX



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Effect of magnetic interactions on the magnetic properties of ball-milled $\text{SmCo}_5 + \text{NiO}$ powders

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Abstract

An enhancement of the coercivity, H_C , has been observed in SmCo_5 when ball-milled with antiferromagnetic NiO powders. Moreover, after short-term milling, these composites exhibit very high values of the squareness without need for particle alignment. Classical ΔM plots show that short-range exchange interactions are predominant for fields $H < H_C$, while long-range magnetostatic interactions prevail for $H > H_C$. © 2002 Published by Elsevier Science B.V.

Keywords: Remanence; Interaction effects; Antiferromagnets; Coercivity

Isotropic nanocrystalline hard magnetic materials produced by ball-milling usually exhibit values of the squareness ratio, M_R/M_S (remance/saturation magnetization), larger than the value of 0.5 predicted by the non-interacting single-domain particles model [1]. This enhanced remanence behavior is usually attributed to short-range exchange interactions between the ferromagnetic (FM) grains [2] and has been observed both in single phase [3] and in spring-magnets [4]. Moreover, long-range dipolar interactions, which have a net demagnetizing effect, are also frequently present between magnetic particles. To investigate the nature of the magnetic interactions between the different FM grains, a procedure known as ΔM plot was developed [5]. ΔM is defined as $\Delta M = M_d(H)/M_r(\infty) - (1 - 2M_r(H)/M_r(\infty))$, where $M_r(H)$ is the isothermal remanent magnetization, $M_r(\infty)$ is the remanent magnetization after fully saturating the sample and $M_d(H)$ is the demagnetization remanence. Usually, positive ΔM are interpreted as magnetizing exchange interactions, while negative ΔM corresponds to demagnetizing-like magnetostatic interactions. Furthermore, exchange interactions between FM and antiferromagnetic (AFM) materials are known to result in an enhancement of the coercivity, H_C (for a recent review see Ref. [6]) [7].

However, the effect of these interactions in the squareness of FM–AFM systems is less understood. In this study various types of magnetic interactions arising at the different stages of the milling process in SmCo_5 ball-milled with NiO (AFM with Néel temperature $T_N = 590$ K) are evaluated using standard ΔM plot procedures.

Ball-milling of SmCo_5 (99%, $< 500 \mu\text{m}$) with NiO (99%, $< 44 \mu\text{m}$) in a weight ratio of 1:1 has been carried out for different times (0.25–32 h) in a planetary ball-mill, under argon atmosphere, in agate vials and balls (6), with a ball to powder weight ratio of 2:1. Structural characterization was performed by X-ray diffraction, where the patterns were fitted using the Rietveld method [8], and the grain sizes and microstrains were also determined. The morphology was observed by scanning electron microscopy (SEM). Magnetic hysteresis loops and ΔM plots were carried out on tightly packed isotropic powders by means of an extracting magnetometer, with a maximum applied field of 20 T.

As the milling proceeds, SmCo_5 and NiO particles both tend to reduce their size. At the same time, SmCo_5 particles acquire a more regular shape and progressively become embedded in an AFM NiO matrix [9]. This microstructure, which allows the existence of a large number of interfaces between SmCo_5 and NiO , is very favorable for the magnetic exchange interactions between both components. Moreover, the crystallite size is

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found to steadily decrease with milling time, while the microstrains increase drastically for long milling times.

Fig. 1 shows the demagnetization curves and (inset) squareness ratio for $\text{SmCo}_5 + \text{NiO}$ ball-milled for different times. The systematic milling time dependences of H_C for SmCo_5 , $\text{SmCo}_5 + \text{NiO}$ and $\text{SmCo}_5 + \text{CoO}$ have been reported elsewhere [10]. Briefly, after short-term milling H_C increases for all systems. However, although a maximum of $\mu_0 H_C = 1.1 \text{ T}$ is observed after 4 h in SmCo_5 , H_C continues to increase steadily with the milling time for ball-milled $\text{SmCo}_5 + \text{NiO}$, reaching a value of $\mu_0 H_C = 1.5 \text{ T}$ after 32 h of milling (i.e. larger than the maximum coercivity of SmCo_5 milled alone). Nevertheless, H_C for $\text{SmCo}_5 + \text{CoO}$ (CoO behaves paramagnetically at room temperature) remains at about $\mu_0 H_C = 1.1 \text{ T}$ even for long milling times (i.e. similar to the maximum $\mu_0 H_C$ for SmCo_5 milled alone). This indicates that such H_C enhancement is, at least in part, related to FM–AFM exchange interactions between SmCo_5 and NiO particles, which becomes progressively more important as the milling time is increased [10]. Moreover, a sharp increase of M_R/M_S is observed in ball-milled isotropic SmCo_5 powders after short-term milling (e.g. $M_R/M_S = 0.9$ after 1 h). Several models have shown that short-range exchange interactions between the different FM particles can produce an increase of M_R [2]. Hence, it would be expected that when SmCo_5 particles are ball-milled with a non-ferromagnetic material, the FM–FM exchange interactions would tend to decrease, since the role of the non-ferromagnetic material would be to isolate the different SmCo_5 grains. In fact, this is what has been observed in ball-milled $\text{SmCo}_5 + \text{CoO}$, where $M_R/M_S = 0.85$ after milling for 1 h. Nevertheless, M_R/M_S is found to be further enhanced in ball-milled $\text{SmCo}_5 + \text{NiO}$

($M_R/M_S = 0.98$ after milling for 1 h), indicating that FM–AFM interactions could also play some role in enhancing M_R/M_S . Increases in M_R/M_S have occasionally been reported in other AFM–FM systems [11]. It is noteworthy that when the milling time is further increased, M_R/M_S tends to decrease in both SmCo_5 and $\text{SmCo}_5 + \text{NiO}$. However, M_R/M_S remains larger in $\text{SmCo}_5 + \text{NiO}$ for all milling times (e.g. after milling for 32 h, $M_R/M_S = 0.67$ for $\text{SmCo}_5 + \text{NiO}$ while $M_R/M_S = 0.58$ for SmCo_5).

Fig. 2 shows the ΔM plots for $\text{SmCo}_5 + \text{NiO}$ ball-milled for 1, 4 and 32 h. It can be seen that both types of interactions (magnetostatic and exchange) are present in the system. Positive ΔM values are obtained when the applied field is lower than H_C , while magnetostatic interactions are predominant for $H > H_C$. Similar ΔM plots have also been reported for spring-magnets, where M_R/M_S is also enhanced when comparing with the hard component [12].

A simpler way to quantify the strength of the interactions using a single parameter is the so-called interaction field factor (IFF), which is defined from H_C and the remanence coercivities, H_r and H'_r (where $M_d(H_r) = 0$ and $M_r(H'_r) = 1/2$), as follows: $\text{IFF} = [(H'_r - H_r)/H_C] \times 100$ [13]. IFF would be expected to be zero for non-interacting single domain particles and to increase as the interactions become more important. Table 1 shows the milling time dependences of IFF, as well as those of the SmCo_5 crystallite size ($\langle D \rangle_{\text{SmCo}_5}$), NiO crystallite size ($\langle D \rangle_{\text{NiO}}$), SmCo_5 microstrain ($\langle \epsilon^2 \rangle^{1/2}$), H_C and M_R/M_S for ball-milled $\text{SmCo}_5 + \text{NiO}$.

As can be seen in Fig. 2, magnetostatic interactions (i.e. the negative peak in the ΔM plots) tend to decrease as the milling time is increased. This can be due to the

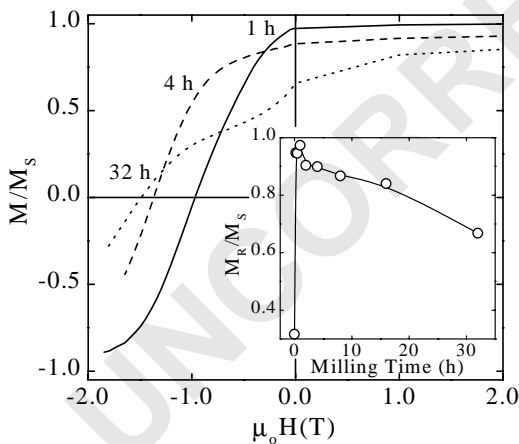


Fig. 1. Normalized demagnetization curves for $\text{SmCo}_5 + \text{NiO}$ ball-milled for 1 h (—), 4 h (---) and 32 h (·····) and (inset) squareness ratio, M_R/M_S , for $\text{SmCo}_5 + \text{NiO}$ ball-milled for different times (0.25–32 h).

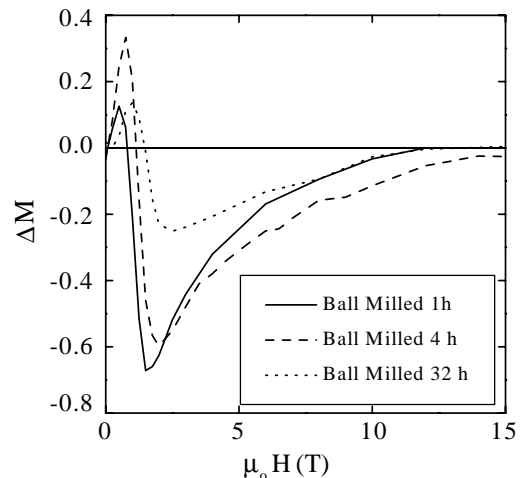


Fig. 2. ΔM plots for $\text{SmCo}_5 + \text{NiO}$ ball-milled for 1 h (—), 4 h (---) and 32 h (·····).

Table 1
Summary of the structural and magnetic properties for SmCo₅+NiO ball-milled for 1, 4 and 32 h

| Milling times (h) | $\langle D \rangle_{\text{SmCo}_5}$ (nm) | $\langle D \rangle_{\text{NiO}}$ (nm) | $\langle e^2 \rangle^{1/2}$ | $\mu_0 H_C$ (T) | M_R/M_S | IFF (%) |
|-------------------|--|---------------------------------------|-----------------------------|-----------------|-----------|---------|
| 1 | 20 | 27 | 0.004 | 1.13 | 0.98 | 38.3 |
| 4 | 18 | 22 | 0.007 | 1.33 | 0.90 | 16.1 |
| 32 | 9 | 11 | 0.011 | 1.50 | 0.67 | 10.8 |

homogenization of SmCo₅ particles during the milling. In fact, the SEM investigations reveal that the starting SmCo₅ particles are of rather irregular shapes, and have sizes of up to 200 μm. These particles, apart from probably being multidomain, can give rise to strong stray fields, especially at sharp corners that tend to demagnetize the neighboring particles, thus enhancing dipolar interactions and giving low values of M_R/M_S on the unmilled SmCo₅ particles (see inset in Fig. 1). However, ΔM plots indicate that dipolar interactions are still present after even long-term milling. The milling time dependence of the exchange interactions is somewhat more complex. As seen in Fig. 2, although the field range in which exchange interactions predominate increases with the milling time, the highest positive peak in the ΔM plots is observed after 4 h of milling. However, IFF is maximum after 1 h of milling. This unusual behavior could be interpreted in terms of the interplay between the FM–FM and the AFM–FM exchange interactions. As mentioned, M_R/M_S reaches its maximum value after 1 h of milling and it reduces slowly for longer milling times. This indicates that exchange interactions between FM grains have their maximum effect after 1 h of milling and tend to decrease afterwards, probably due to the introduction of large amounts of defects, such as dislocations or stacking faults, during the milling (see high microstrain values in Table 1), which reduce the size of the exchange coupled regions in the FM. This correlates well with the milling time dependence of IFF. However, exchange interactions between the FM and the AFM particles are expected to increase with the milling time, since prolonged milling allows a larger amount of interfaces to be formed between SmCo₅ and NiO. Thus, the competition between the FM–FM and the FM–AFM exchange interactions, which have opposite tendencies during the milling, could explain the non-monotonic behavior of the positive peak in the ΔM plots. However, due to the interplay among FM–FM exchange and dipolar interactions and the AFM–FM exchange, the detailed correlation between M_R/M_S enhancement and the ΔM plots is found to be rather complex.

In conclusion, we have shown that an enhanced H_C and very high values of M_R/M_S can be obtained in

isotropic ball-milled SmCo₅+NiO. ΔM plots show that the strong exchange interactions, either between the different FM or between the FM and AFM grains, observed predominantly for fields $H < H_C$, can be responsible for these effects. ΔM plots also indicate that dipolar interactions become predominant for $H > H_C$. However, these demagnetizing interactions are shown to decrease with milling time.

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