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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-

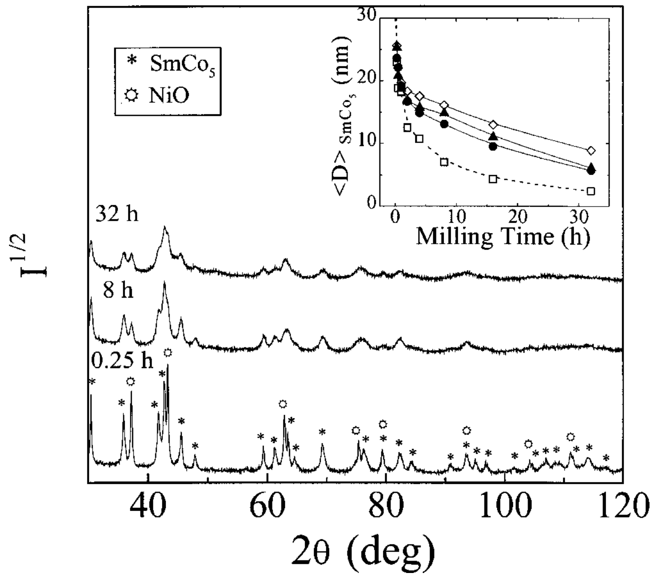

FIG. 1. XRD patterns of $SmCo_5$ milled with NiO during 0.25, 8, and 32 h in the weight ratio of 3:1. In the inset, milling time dependence of the $SmCo_5$ crystallite size $\langle D\rangle_{\mathrm{SmCo5}}$ for the $SmCo_5$:NiO weight ratios 1:0 (--□--), 3:1 (—●—), 3:2 (—▲—), and 1:1 (—◇—). Note that, for clarity, the crystallite size of the starting $SmCo_5$ powders (i.e., $\langle D\rangle_{\mathrm{SmCo5,initial}}=43$ nm) has not been plotted. The lines are a guide to the eye.

netometer, with a maximum applied field of $\mu_0H=23$ T, in tightly packed isotropic powders. The angular dependence of the magnetization was measured using vector magnetometry in a field of $\mu_0H=5$ T, in oriented powders embedded in resin.

Shown in Fig. 1 are the XRD patterns of $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ crystallite size $\langle D\rangle_{\mathrm{SmCo5}}$ is shown for different NiO contents. For all compositions, $\langle D\rangle_{\mathrm{SmCo5}}$ is found to decrease steeply for short milling times ($\langle D\rangle_{\mathrm{SmCo5}}=43$ 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_{SmCo5} (32 h)$\sim 3\times10^{-3}$, $\alpha_{\mathrm{SmCo5+NiO}}$ (32 h)$\sim 1\times10^{-3}$]. 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 $SmCo_5$:NiO ratios during the milling (e.g., $\langle\epsilon^2\rangle^{1/2}\sim 8\times10^{-3}$ 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 $SmCo_5$ is milled with NiO, the crystallite size reduction due to the milling becomes smoother. These results clearly show that NiO slows down $SmCo_5$ crystallite size refinement induced during the milling.[9]

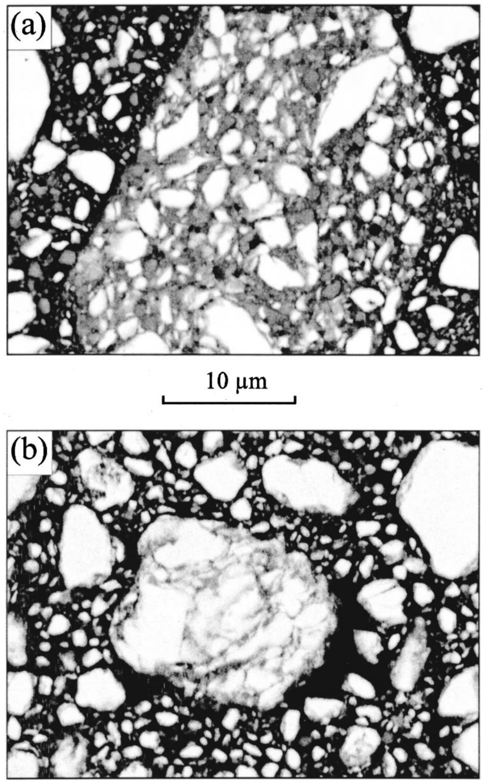

FIG. 2. SEM images (backscattered electrons) of $SmCo_5$ milled with NiO during 16 h in the weight ratios of (a) 1:1 and (b) 3:1. The bright particles correspond to $SmCo_5$ while the gray areas to NiO. Note that the black regions are epoxy resin.

Shown in Fig. 2 are scanning electron microscopy (SEM) images (backscattered electrons) of $SmCo_5$ 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 $SmCo_5$, while the gray zones correspond to NiO (the black regions are epoxy resin). The original $SmCo_5$ 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 $SmCo_5$ is milled with NiO. After short-term milling the powders mix and the crystallite size is reduced. However, as the milling proceeds, $SmCo_5$ 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 $SmCo_5(3)$:(1)NiO agglomerates larger that 15 μm are rarely obtained. Furthermore, the

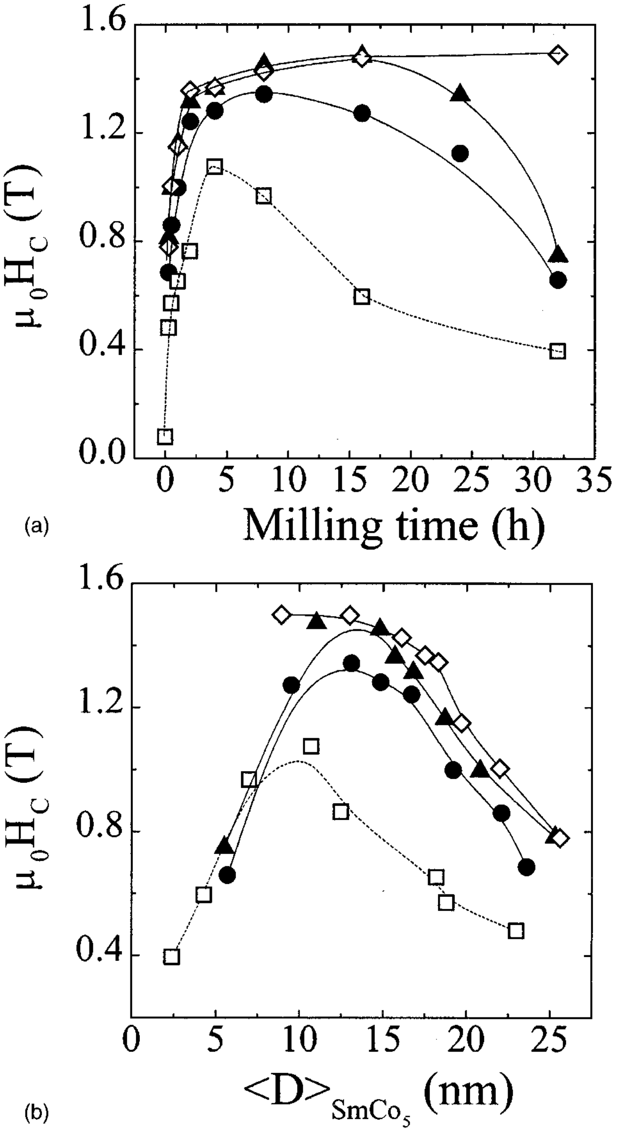

FIG. 3. (a) Milling time dependence of the coercivity $\mu_0 H_C$ for $SmCo_5$ milled with NiO in the weight ratios 1:0 (--□--), 3:1 (—●—), 3:2 (—▲—), and 1:1 (—◇—). (b) Dependence of $\mu_0 H_C$ on the $SmCo_5$ crystallite size $\langle D \rangle_{SmCo5}$, for $SmCo_5$ milled with NiO in the same weight ratios. Note that, for clarity, the value of $\mu_0 H_C$ for the starting $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ 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 $\langle D \rangle_{SmCo5}$, of around 10 nm, in good agreement with other works on ball milled $SmCo_5$.[15] Nevertheless, when $SmCo_5$ 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, $SmCo_5$ 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 $SmCo_5$ is milled with NiO a remarkable enhancement of $\mu_0 H_C$ is obtained, e.g., $H_C = 1.5$ T in $SmCo_5$ (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 $SmCo_5$ and NiO. Namely, the magnetocrystalline anisotropy of NiO is exceedingly small to allow for the existence of significant loop shifts when coupled to $SmCo_5$. Furthermore, $SmCo_5$ is known to undergo structural transitions when heated,[2] 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 $SmCo_5 + NiO$ 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 $SmCo_5$ milled alone. At room temperature [i.e., above the $T_N(\mathrm{CoO}) = 290$ K] the role of CoO is to merely separate the $SmCo_5$ particles, thus reducing the exchange interactions between them. The fact that H_C is larger for $SmCo_5 + NiO$ than for $SmCo_5 + CoO$ for all milling times indicates that the role of NiO (AFM at room temperature) is more than to simply separate the $SmCo_5$ particles. Moreover, if in the $SmCo_5 + CoO$ system the temperature is reduced to below CoO T_N ($\sim$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 $\langle D\rangle_{\mathrm{SmCo5}}$ 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 $\mathrm{SmCo_5+CoO}$ remained always between those of $\mathrm{SmCo_5}$ and $\mathrm{SmCo_5+NiO}$.[6] Moreover, contrary to what has been observed for the crystallite size, $\langle D\rangle_{\mathrm{SmCo5}}$, 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 $\mathrm{SmCo_5}$ or isolate the different $\mathrm{SmCo_5}$ 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 $\mathrm{SmCo_5}$ 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 $\mathrm{SmCo_5}$ 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 $M_R/M_S(\mathrm{SmCo_5})\approx 0.9$, 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 $\mathrm{SmCo_5}$ alone [e.g., after 16 h of milling $M_R/M_S(\mathrm{SmCo_5})\approx 0.6$, $M_R/M_S(3{:}1)\approx 0.7$, $M_R/M_S(3{:}2)\approx 0.75$, 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 $(\mathrm{BH})_{\max}$, 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 $(\mathrm{BH})_{\max}$.[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 $(\mathrm{BH})_{\max}$ is shown for different AFM:FM ratios. It can be observed that the dependence of $(\mathrm{BH})_{\max}$ on the AFM content is rather complex. This is because of the opposing effects of the AFM in the enhancement of $(\mathrm{BH})_{\max}$. On the one hand, both H_C and M_R/M_S increase 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 $(M_{\mathrm{AFM}}=0)$, which does not contribute to the overall saturation magnetization. Consequently, as seen in Fig. 4, $(\mathrm{BH})_{\max}$ is reduced when the NiO content is increasingly high, as, for example, in the case of the 1:1 ratio. Nevertheless, $(\mathrm{BH})_{\max}$ for the $\mathrm{SmCo_5}$ (3):(1) NiO milled for 4 h exhibits an enhancement with respect to the maximum of pure $\mathrm{SmCo_5}$. Therefore, due to the interplay of all the different effects, an enhancement of $(\mathrm{BH})_{\max}$ can only be achieved through the optimization of the FM: AFM ratio and processing conditions.

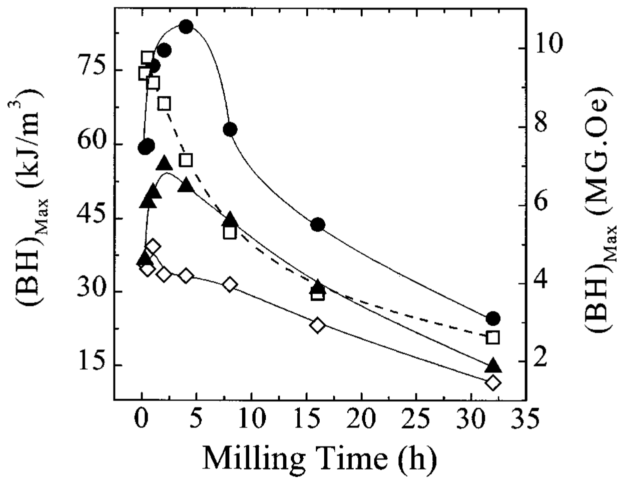

FIG. 4. Milling time dependence of the energy product $(\mathrm{BH})_{\max}$, for $\mathrm{SmCo_5}$ milled with NiO in the weight ratios 1:0 (--□--), 3:1 (—●—), 3:2 (—▲—), and 1:1 (—◇—). Given on the right axis are the $(\mathrm{BH})_{\max}$ values in cgs units. Note that the error bars are smaller than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

In conclusion, we have shown that by ball milling a hard magnetic material, such as $\mathrm{SmCo_5}$, 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 $M_{\mathrm{AFM}}=0$ 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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