Chapter 3

Articles

Article I

Room-temperature coercivity enhancement in mechanically alloyed antiferromagnetic-ferromagnetic powders

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The coercivity, H_C, and squareness of Co powders have been enhanced at room temperature by mechanically alloying them with antiferromagnetic powders with Néel temperature, T_N, above room temperature. The enhancement is maximum after field annealing above T_N. The existence of loop shifts and the dependence of H_C on the annealing and measuring temperatures indicate that exchange bias effects are responsible for this behavior. © *1999 American Institute of Physics.*
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Direct or indirect exchange interactions between magnetic materials have produced a wide range of interesting properties, such as giant magnetoresistance (GMR)[1,2] in magnetic multilayers, remanence enhancement in magnetically soft-hard composite permanent magnets[3,4] or exchange bias in ferromagnetic (FM)—antiferromagnetic (AFM) structures.[5,6] In particular, exchange bias has been widely studied in thin films, where numerous possible combinations of AFM-FM (or ferrimagnetic), have been investigated.[6] However, in fine particles, basically transition metal particles (Fe, Co, Ni, or their alloys) embedded in their AFM (or ferrimagnetic) native oxides (e.g., FeO,[7] Fe_3O_4,[8,9] CoO,[5,10] or NiO[9,11]) or surrounded by chemically obtained sulfides (FeS[12]) or nitrides (CoN,[13] Fe_2N[8]), have been studied. Moreover, recently, exchange coupling of fine powders obtained by mechanically alloying transition metals (Fe, Co, Ni) and their antiferromagnetic oxides (CoO or NiO) or sulfides (FeS) has also been carried out.[14] It is noteworthy that all the fine particle systems studied up to date consist of FMs and AFMs of the *same* transition metal, e.g., Fe and Fe-based AFMs (FeO, FeS, Fe_2N).[5–14] Although, as observed in thin films, many fine particle systems exhibit loop shifts, the aspect of exchange bias most studied in fine particles is the enhancement of the coercivity.[6] However, this enhancement is mainly observed at low temperatures, either because the AFM shells have T_N below room temperature (FeO, CoO) or the shells are so thin that they behave superparamagnetically at room temperature.[5,8–11,13]

In this letter, we report the enhancement of the coercivity at room temperature for mechanically alloyed FM-AFM powders of *different* transition metals, Co–NiO and Co–FeS, after appropriate heat treatments.

Mechanical alloying of the FM-AFM powders was carried out for different times (0.1–30 h) using a planetary mill in agate vials ($V=20$ ml) and six 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 starting materials were powders of Co (99.5%, <44 μm), NiO (99%, <44 μm), and FeS (95%, <100 μm), where NiO and FeS are AFM with Néel temperatures around

$T_N=590$ K and $T_N=610$ K, respectively.[15] The weight ratio of FM to AFM was usually kept to 1:1. Ball milling of pure Co powder was also carried out in the same conditions. The as-milled powders were annealed for different times in vacuum, under different magnetic fields ($H=0–10$ kOe), in the range of 300–850 K and field cooled to room temperature. The samples were structurally characterized by x-ray diffraction, using a Cu $K\alpha$ incident radiation. Magnetic hysteresis loops, up to 10 kOe, were carried out in loosely packed powders at room temperature by means of vibrating sample magnetometry (VSM).

As can be seen in Fig. 1, as the milling time increases, the coercivity (H_C) of the pure Co samples increases, up to 1 h. This initial H_C increase is due to the transformation of the original fcc+hcp powder to hcp, as observed by x-ray diffraction,[16,17] where pure hcp-Co is known to have larger H_C than fcc-Co.[18] Further increase of the milling time causes
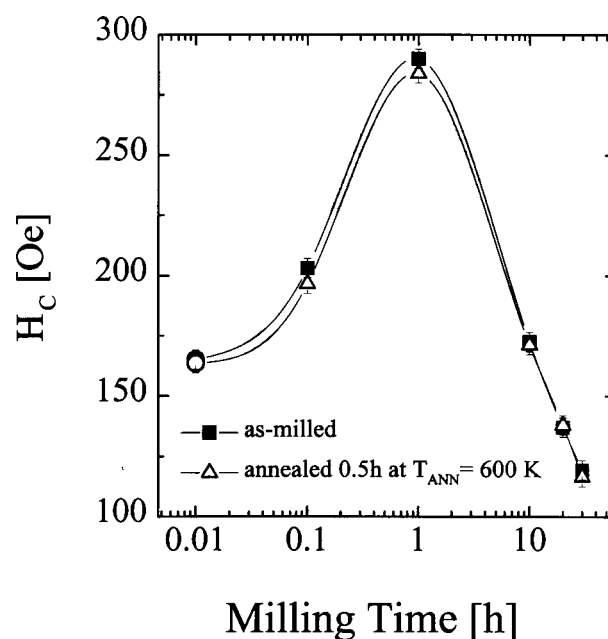

FIG. 1. Dependence of the coercivity, H_C, on the milling time for Co powders for as milled (full symbols) and milled and annealed at $T_{ANN}=600$ K for 0.5 h at $H=5$ kOe (open symbols). Note that the circles are for the original Co powders, as-obtained (full symbol) and annealed at $T_{ANN}=600$ K for 0.5 h (open symbols). The lines are a guide to the eye.
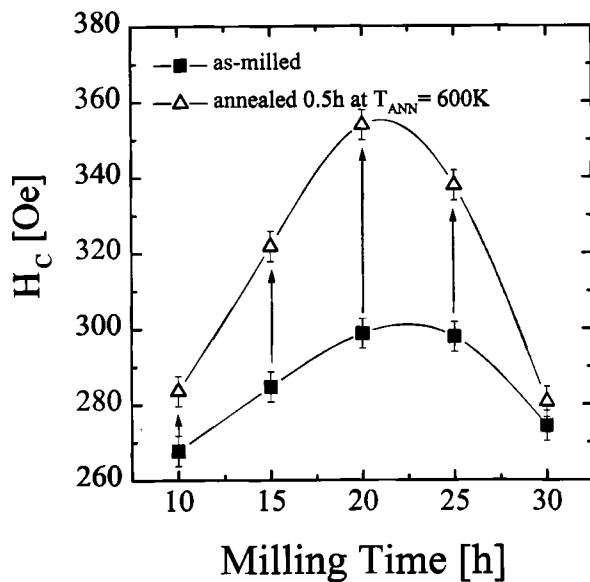
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FIG. 2. Dependence of the coercivity, H_C, on the milling time for Co–NiO 1:1 powders for as milled (full symbols) and milled and annealed at T_{ANN} = 600 K for 0.5 h at H = 5 kOe (open symbols). The lines are a guide to the eye.

FIG. 3. Dependence of the coercivity, H_C, on the annealing temperature, T_{ANN}, for Co–NiO 1:1 powders milled for 20 h and annealed during 0.5 h at H = 5 kOe. Shown in the inset are the dependence of the loop shift in the field axis, H_E (full symbols), and the squareness, M_R/M_S (open symbols) on the annealing temperature, T_{ANN}. The lines are a guide to the eye.

a reduction of H_C (Fig. 1). This effect is probably linked with the transformation of hcp-Co to a random close-packed phase upon long term milling.[16,17] Annealing the as milled powders at 600 K for 0.5 h produces a slight decrease in H_C (Fig. 1) which is probably related to grain growth and/or initial transformation of the hcp-Co to fcc-Co during the annealing.

Similar to what is observed for ball milled pure Co, a maximum in H_C is also obtained for mechanically alloyed Co–NiO particles when increasing the milling time, as shown in Fig. 2. Nevertheless, the maximum appears now for much longer milling times, i.e., 20 h. Hence, NiO slows down the Co phase transformation during mechanical alloying. Contrary to what we observe for ball milled Co, annealing at 600 K for 0.5 h in a field of H = 5 kOe, produces a significant increase in H_C. Thus, the addition of NiO particles in the mechanical alloying plays an important role in the enhancement of H_C. To better understand the role of NiO, annealings at other temperatures have been carried out. As can be observed in Fig. 3, the maximum effect is found around T_{ANN} = 600 K, i.e., for $T_{ANN} > T_N$. However, if T_{ANN} is too high there is a transformation from hcp-Co to fcc-Co, causing the reduction of H_C. The enhancement of H_C after field cooling through the Néel temperature is in agreement with what is found for fine powder systems at low temperatures.[6] Therefore, these results seem to indicate that it is the exchange interaction-exchange bias between the AFM and FM powders which induces the coercivity enhancement.

To confirm this assumption, we carried out annealings at different fields. As expected, annealing at H = 0 kOe also produces an increase in H_C due to the remanence of the Co powders which create a field to the NiO powders, in agreement with previous FM-AFM ball milling studies.[14] However, the increase in H_C is 50% smaller than the one obtained for annealing at H = 5 kOe. Annealing time is also found to play an important role. Long annealing times (several hours)
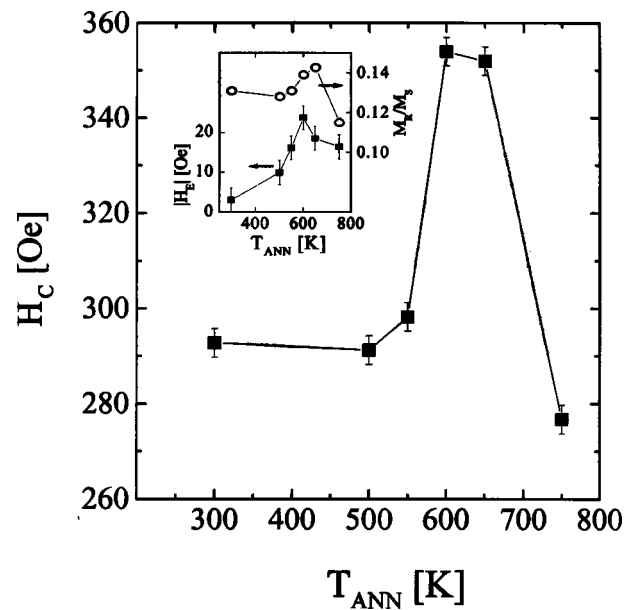
tend to either slowly transform hcp-Co towards fcc-Co and/or probably induce excessive interdiffusion, leading to a decrease of the H_C enhancement. In our case, for the sample mechanically alloyed for 20 h annealing for more than 3 h was found to deteriorate the properties. The maximum coercivity increase found in this study was around 125% ($H_{C,Max}$ = 370 Oe), with respect to the original Co powder.

Further evidence for the origin of the increase in H_C comes from the shift, towards negative fields, in the hysteresis loop along the field axis, H_E (Fig. 3), which is typically induced by AFM-FM exchange coupling.[6] In agreement with Ni–NiO fine powder studies[9,11] and Co–NiO thin film studies,[19] the loop shifts observed for the Co–NiO samples mechanically alloyed for 20 h are rather small as compared to their coercivity (see inset of Fig. 3). This is probably due to the rather small anisotropy of NiO, which causes the AFM spins to be easily rotated by the FM spins, thus inducing a small loop shift but a large coercivity.[5,6] The system exhibits its maximum loop shift at T_{ANN} = 600 K in agreement with H_C (Fig. 3).

An enhancement in the squareness ratio, M_R/M_S, where M_R and M_S are the remanent and saturation magnetization, is also observed after field annealing the Co–NiO powders. The increase in M_R/M_S follows the same behavior as H_C with annealing (see Fig. 3 inset), with a maximum enhancement of remanence of $M_R/M_S \approx 70\%$ as compared to the original Co powder. The origin of this enhancement of the remanence is still not well understood. However, its T_{ANN} dependence indicates that it is also related to exchange bias.

Finally, we have also observed that all the above effects (enhancement of H_C and M_R and loop shift) obtained after annealing at T_{ANN} = 600 K and field cooling to room temperature, decrease for increasing measuring temperatures,
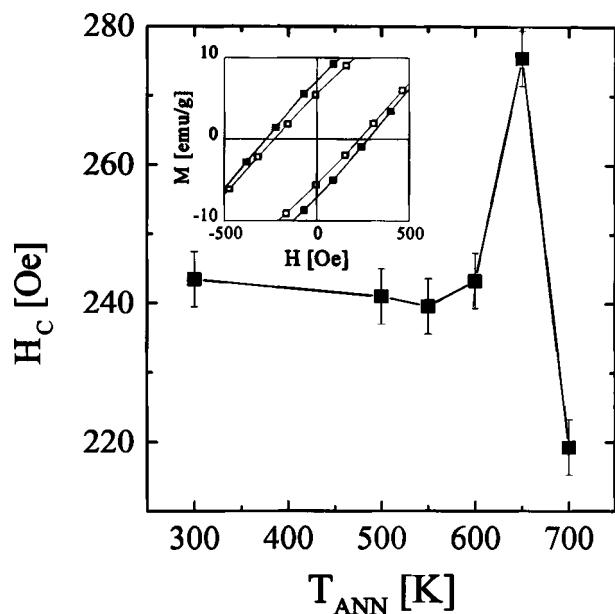
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Sort *et al.* 3179

FIG. 4. Dependence of the coercivity, H_C, on the annealing temperature, T_{ANN}, for Co–FeS 1:1 powders milled for 10 h and annealed during 0.1 h at $H = 5$ kOe. Shown in the inset are the hysteresis loops of the as-milled sample (open symbols), and the sample annealed at $T_{ANN} = 650$ K for 0.1 h (full symbols). The line is a guide to the eye.

disappearing above T_N, as expected for exchange bias effects.[6]

Mechanical alloying of Co–FeS leads to a similar increase in the H_C and the presence of loop shifts (an example of the comparison of the hysteresis loops before and after field annealing is shown in the inset of Fig. 4). However, the maximum in H_C is not observed after field annealing at $T_{ANN} = 600$ K, as for NiO, but at $T_{ANN} = 650$ K (see Fig. 4), i.e., for $T_{ANN} > T_N = 613$ K. This provides further evidence for the exchange interaction between the FM and AFM induced when field cooling through the Néel temperature of the AFM.

In conclusion, we have shown an enhancement of the coercivity and squareness ratio of Co powders at room temperature and above, by mechanically alloying them with NiO and FeS. The coercivity of the Co–NiO powders exhibits a maximum at longer milling times than for pure Co. Moreover, field annealing increases H_C rather than decreasing it, as observed for pure Co. The maximum enhancement of H_C is found for field annealing at $T_{ANN} > T_N$ and posterior field cooling to room temperature. The hysteresis loops also ex-

hibit shifts in the field axis. The effects disappear for measuring temperatures above T_N. This behavior indicates that the H_C enhancement is caused by exchange bias effects. In agreement with thin film systems, exchange bias properties can be obtained in fine powders composed of FM and AFM of different transition metals. Moreover, being able to increase and control H_C at room temperature and above makes these materials interesting for magnetic applications. In particular, hard magnets (FeNdB, SmFe) could be mixed (e.g., mechanically alloyed) with AFMs with T_N above room temperature to further enhance their coercivity.

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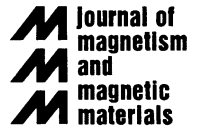[18] H. Sato, O. Kitakami, T. Sakurai, Y. Shimada, Y. Otani, and K. Fukamichi, J. Appl. Phys. **81**, 1858 (1997).
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Article II

Room temperature magnetic hardening in mechanically milled ferromagnetic–antiferromagnetic composites

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Abstract

Enhancements in coercivity, squareness and energy product have been obtained at room-temperature by mechanically milling mixtures of ferromagnetic (FM) (Co) and antiferromagnetic (AFM) (NiO) powders. All these effects decrease with increasing temperatures, up to $T = 600$ K, just above the Néel temperature of the antiferromagnet. Due to the competition between coercivity enhancement and reduction of saturation magnetization in AFM/FM mixtures, although the maximum coercivity enhancement has been found for (AFM)1:1(FM) weight ratio, the maximum energy product is obtained for composites with larger FM content, i.e. (AFM)2:3(FM). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Coercivity; Energy product; Exchange bias; Ferromagnetic–antiferromagnetic; Ball milling

Mechanical alloying of soft and hard magnetic materials introduces exchange interactions between both materials, which have been used to induce magnetic hardening in magnetic materials [1,2]. The exchange interaction creates a remanence increase in the hard magnetic materials, which leads to the enhancement of the energy product, BH_{max}. Similar effects have also been found in soft–hard bilayer and multilayer systems [3]. Exchange interactions between ferromagnetic (FM) and antiferromagnetic (AFM) materials have been mainly studied in thin film systems [4–6] and transition metal particles embedded in their native oxides [4,7–9]. These systems exhibit loop shifts in the field axis and a coercivity enhancement, as they are field cooled through the Néel temperature of the AFM, T_N [4]. In fine particle systems, these effects are usually present only far below room temperature [4,7–9]. Although the microscopic origin of the loop shifts and coercivity enhancements is not clear at present, simple models [7,8] suggest that AFM materials with larger anisotropies tend to induce larger loop shifts, while AFM with smaller anisotropy bring about important coercivity enhancements [4].

We have recently shown that it is possible to enhance the room-temperature coercivity of FM materials by heat treating mechanically milled ferromagnetic–antiferromagnetic composites, such as Co–NiO or Co–FeS [10].

In this paper we study the optimal conditions (AFM:FM ratio, milling time) for room-temperature enhancement of the *energy product*, BH_{max}.

The BH_{max} enhancement is found to be maximum for (AFM) 2 : 3 (FM) and disappears above the AFM Néel temperature, as expected for AFM–FM exchange interaction effects.

Mechanical milling of mixtures of gas-atomized powders of FM Co (99.5%, $< 44 \, \mu m$, $T_C =$ 1404 K) and AFM NiO (99%, $< 100 \, \mu m$, $T_N =$ 590 K) was carried out for different times (0.1–30 h), at 500 rpm by means of a planetary mill, using agate vials ($V = 20 \, ml$) and six agate balls ($\phi = 10 \, mm$). The ball to powder weight ratio was kept to 2 : 1. Different AFM : FM weight proportions were studied: 0 : 1, 3 : 7, 2 : 3, 1 : 1 and 3 : 2. To induce exchange coupling between AFM and FM phases [4], the as-milled powders were annealed under vacuum, above T_N, at $T_{ANN} = 600 \, K$ ($T_N < T_{ANN} < T_C$), for 0.5 h, in the presence of a $H = 5 \, kOe$ magnetic field and field cooled to room temperature.

The samples were structurally characterized by X-ray diffraction (XRD) (Cu-K_α-radiation). Their morphological characterization was performed by using scanning electron microscopy (SEM), equipped with energy dispersive X-ray analysis (EDX). Magnetic hysteresis loops, up to 10 kOe, were measured in loosely packed powders, at temperatures between room temperature and 750 K, by means of vibrating sample magnetometry (VSM).

Fig. 1 shows the dependence of the room-temperature coercivity, H_C, on the milling time for the NiO : Co weight ratios of 1 : 1 and 2 : 3 (before and after field annealing). In both the cases, as the milling time increases, a maximum in H_C is obtained. The initial H_C rise is attributed to the transformation of the original mixture of FCC and HCP-Co to HCP at the first stages of milling, as has been observed by XRD [11,12]. The reduction of H_C after the long-term milling is probably linked with the transformation of the HCP-Co to a random close packed phase [11,12]. As can be observed in Fig. 1, after field annealing at $T_{ANN} =$ 600 K in $H = 5 \, kOe$ and field cooling to room temperature, both AFM : FM ratios exhibit an enhancement of the coercivity (defined as the difference of H_C before and after annealing, ΔH_C). A summary of the room-temperature data for the different NiO : Co exchange couples is presented in Table 1. Coercivity enhancements and loop shifts in
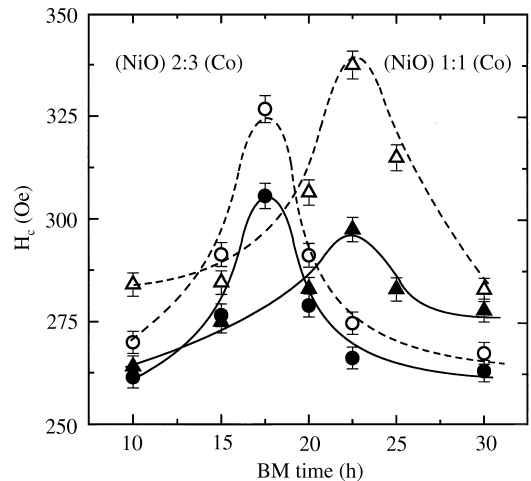

Fig. 1. Dependence of the room-temperature coercivity, H_C, on the ball milling (BM) time for (NiO)2 : 3(Co) (-○-) and (NiO)1 : 1(Co) (-△-) weight ratios, as-milled (filled symbols) and after (open symbols) field annealing ($H = 5 \, kOe$) at $T_{ANN} =$ 600 K for 0.5 h.

the field axis, H_E, towards the negative field axis, are observed for all AFM/FM ratios (except in pure Co) after annealing at $T_{ANN} = 600 \, K$ and field cooling to room temperature. This is expected from exchange interactions between the FM and the AFM. Simple models [4,7,8] suggest that when a system consisting of an FM and an AFM is field cooled through T_N, the spins of the AFM tend to align ferromagnetically to the spins of the FM, inducing an interface coupling. Consequently, when a hysteresis loop is performed on the AFM–FM coupled system, as the FM spins try to rotate they have to 'drag' irreversibly by the AFM spins due to the coupling (for systems with small AFM anisotropy); thus increasing H_C. In addition, due to the AFM–FM coupling, an unidirectional anisotropy is introduced in the system, which is the origin of the shift of the hysteresis loop [4,7,8]. As can be seen in Table 1, the maximum coercivity enhancement, ΔH_C, is obtained for the 1 : 1 weight ratio, where ΔH_C is about 45 Oe. Note that the maximum H_C after milling was also observed for the 1 : 1 weight ratio (Table 1). Also shown in Table 1 is the required milling time so as to achieve the largest coercivities, t_{max}, for the different NiO : Co weight ratios. As the Co content

Table 1
Summary of the room-temperature magnetic properties of ball-milled NiO : Co mixtures, for different % Co content (in brackets, the NiO : Co weight ratio), where t_{max} is the optimum milling time as to achieve the maximum ΔH_C. All values before annealing (b.a.) and after annealing (a.a.) at $T_{ANN} = 600$ K are given for the optimum t_{max}

% Co content	t_{max} (h)	H_C (t_{max}) (Oe)[b.a.]	H_C (t_{max}) (Oe)[a.a.]	ΔH_C (t_{max}) (Oe)	H_E (t_{max}) (Oe)[a.a.]	$(BH)_{max}$ (G Oe $\times 10^4$)[a.a.]
100 (0 : 1)	1	288 ± 5	284 ± 5	− 4 ± 3	2 ± 3	7.1 ± 0.7
70 (3 : 7)	12.5	280 ± 5	309 ± 5	29 ± 3	8 ± 3	7.6 ± 0.7
60 (2 : 3)	17.5	302 ± 5	330 ± 5	28 ± 3	10 ± 3	8.3 ± 0.7
50 (1 : 1)	22.5	297 ± 5	344 ± 5	47 ± 3	22 ± 3	6.2 ± 0.6
40 (3 : 2)	25	264 ± 5	280 ± 5	16 ± 3	8 ± 3	2.9 ± 0.5

decreases, t_{max} increases. This suggests that NiO probably delays the Co structural changes during the milling. The small values of H_E, as compared to H_C, are attributed to the rather small anisotropy of NiO, which causes the antiferromagnet spins to be easily rotated by the FM spins, thus inducing a small loop shift but a large coercivity [4,7,8]. Moreover, no significant training effect of the loops (i.e. reduction of H_E or H_C for consecutive loops [13]) was observed.

The microstructure of the ball-milled powders helps to better understand the magnetic properties of the FM–AFM system. Short milling times induce mainly mixing of the constituents with only limited contact between NiO and Co. At intermediate milling times, a large number of Co lamellae are formed, which are surrounded by fine particles of NiO. This microstructure induces an increase of the interface area and thus the coupling between the FM and the AFM components [14]. Long milling times probably start to create excessive amounts of defects and intermixing between the AFM and FM phases. It is noteworthy that X-ray results indicate that field annealing ($T_{ANN} < 600$ K) does not induce any phase changes and promotes only minor crystallite growth.

The figure of merit of hard magnetic materials is not so much their coercivity, H_C, as their energy product, BH_{max}. Note that the quality of a permanent magnet is determined by the magnetostatic energy stored in a magnetic circuit containing the magnet. This energy is given by the total area enclosed by the hysteresis loop and is proportional to the area of the maximum rectangle which can be fitted inside the second quadrant of the B–H hysteresis loop. Usually, this 'maximum rectangle' (denoted as BH_{max}) and not the area of the loop, is given as a quantitative measure of the quality of a hard magnet. In Fig. 2, the room-temperature energy products, BH_{max}, are shown as a function of the Co weight percent (AFM/FM ratio). In the as-milled powders, BH_{max} tends to increase as the Co content is raised. Although the maximum H_C after milling remains almost constant for all compositions (see Table 1), the lower saturation magnetization, M_S (defined as the measured magnetic moment divided by the *total* mass (Co + NiO)), for composites with smaller Co content drastically reduces BH_{max}. However, after field annealing ($H = 5$ kOe) the powders at $T_{ANN} = 600$ K and field cooling to room temperature, when exchange interaction is present, an enhancement of the energy product, BH_{max} is obtained. It is remarkable that the highest BH_{max} is found for the 2 : 3 ratio, although H_C was further enhanced in the 1 : 1 samples. The maximum increase of BH_{max} is found to be 83% with respect to the original unmilled Co powder. If the amount of NiO is not large enough (e.g. when the ratio is 3 : 7), the coupling is not so effective in increasing BH_{max}, as can be seen in Fig. 2. If the NiO amount is exceedingly large (e.g. in the ratios 1 : 1 and 3 : 2), the saturation magnetization is excessively reduced, therefore the effect of the increase in H_C due to the coupling is not enough to enhance BH_{max}.

Note that to isolate the effects of the coupling induced by the field cooling, H_C and BH_{max} are given in Fig. 3, for the 1 : 1 ratio, as the difference of
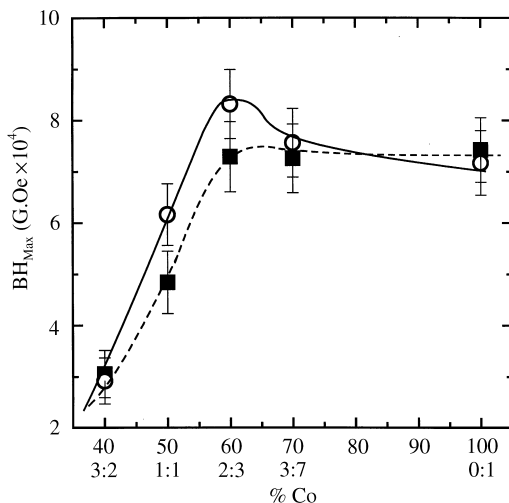
Fig. 2. Dependence of the room-temperature energy product, $BH_{\max}$, on the % Co content (NiO:Co ratio), as-milled (-○-) and after (-■-) field annealing ($H = 5\,\text{kOe}$) at $T_{\text{ANN}} = 600\,\text{K}$ for 0.5 h.

the values after and before the annealing, ΔH_{C} and $\Delta(BH)_{\max}$. As can be seen in Fig. 3, as temperature increases, ΔH_{C}, H_{E} and $\Delta(BH)_{\max}$ all decreases and become almost zero at $T = 600\,\text{K}$. As expected from the nature of the exchange bias coupling, the magnetic hardening (H_{C} and $BH_{\max}$) deteriorates as the temperature is increased. The decrease of these properties with temperature can be understood as a result of a reduction in the AFM/FM interface coupling and as a consequence of either the loss of the magnetic order in the AFM and/or the reduction of the AFM magnetocrystalline anisotropy. The critical temperature at which exchange coupling effects disappear is known as the blocking temperature, usually designed by T_{B}, and is generally close to or below T_{N} [4,15–18]. In most studies concerning exchange coupling in oxidized fine particle systems, T_{B} is far below room temperature. This means that ΔH_{C} and H_{E} are generally only observed at low temperatures [4,6–8]. This is either because T_{N} is below room temperature (e.g. $T_{N}(\text{CoO}) = 290\,\text{K}$ or $T_{N}(\text{FeO}) = 200\,\text{K}$) or because the oxidation of small FM particles leads to surface AFM layers which are either very thin or with very small grains, causing the reduction of T_{N} and thus T_{B} due to finite size effects [4,15–18]. In our case, the NiO crystallites, as deduced from
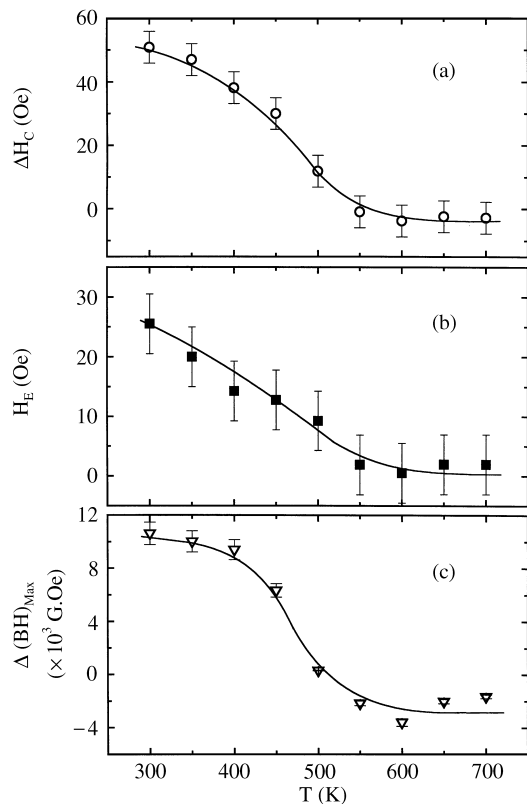

Fig. 3. Temperature dependence of (a) the coercivity enhancement, ΔH_{C}, (b) the loop shift, H_{E} and (c) the enhancement of the energy product, $\Delta(BH)_{\max}$, for the (NiO)1:1 (Co) ratio, ball milled 20 h and field annealed ($H = 5\,\text{kOe}$) at $T_{\text{ANN}} = 600\,\text{K}$ for 0.5 h.

X-ray diffraction, remain rather large ($d \sim 15\,\text{nm}$ [14]), hence $T_{B} \approx T_{N}$.

In conclusion, we have shown that it is possible to enhance the room-temperature coercivity and energy product of a ferromagnet (in our case, Co), by ball milling it with an antiferromagnet, with Néel temperature above room temperature (in our case, NiO). The maximum coercivity, H_{C}, and enhancement of the coercivity, ΔH_{C}, are found for NiO 1:1 Co weight ratio, i.e. when a maximum coupling is present in the system. However, the addition of AFM reduces the overall saturation magnetization in AFM:FM mixtures. As a result, the maximum $BH_{\max}$ is found for NiO 2:3 Co weight ratio and not for NiO 1:1 Co. The enhancement of H_{C} and $BH_{\max}$ are found to

decrease with increasing temperature, vanishing above $T_N(NiO) = 590\,K$, as expected for an exchange coupled FM–AFM system.

Acknowledgements

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