

Article IV

**MAGNETIC HARDENING INDUCED BY EXCHANGE COUPLING IN
MECHANICALLY MILLED ANTIFERROMAGNETIC – FERROMAGNETIC
COMPOSITES**

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ABSTRACT

Mechanical milling has been used to synthesize ferromagnetic (FM, Co) - antiferromagnetic (AFM, NiO) composites. The coercivity, H_C , and energy product, BH_{Max} , of these composites can be enhanced at room temperature after appropriate heat treatments above the Néel temperature of the AFM, T_N . Although the maximum H_C is achieved for the (NiO)1:1(Co) weight ratio, BH_{Max} is further enhanced for the (NiO)2:3(Co) ratio, where higher saturation magnetization is obtained due to the larger amount of FM. Exchange coupling, responsible for these effects, decreases as the temperature is increased and vanishes close to T_N . The thermal stability of the coercivity enhancement remains rather insensitive to the somewhat broad distribution of blocking temperatures of this system.

INTRODUCTION

Since mechanical alloying (MA) was developed in the late 1960s [1], this technique has been used as a processing route for the synthesis of a large variety of equilibrium and non-equilibrium phases and phase mixtures [2]. This technique has been shown to be successful in reducing crystallite sizes to the nanometric range. These small particles can exhibit rather different physical properties from those of their bulk counterpart [3].

Mechanical alloying has also been used to produce direct or indirect magnetic interactions, like in exchange spring magnets (milling soft-hard ferromagnets) [4,5] or giant magnetoresistance materials (milling magnetic-nonmagnetic phases) [6]. However, studies of exchange interaction between ferromagnetic and antiferromagnetic materials induced by ball milling are scarce. Nevertheless, recently the possibility of increasing the room temperature coercivity by mechanical alloying transition metals (Ni, Co, Fe) and their own antiferromagnetic oxides (NiO or CoO) or sulfides (FeS) has been proven [7]. Moreover, it is well known that oxidized ferromagnetic fine particles can also exhibit coercivity enhancements [8]. However, this enhancement is mainly observed far below room temperature, which makes this property not useful for applications. It is noteworthy that coercivity increases due to AFM-FM exchange coupling are also being studied in thin film systems [9,10].

In this paper we show the possibility of increasing the room temperature coercivity and energy product by ball milling FM and AFM composed of *different* transition metals, e.g. Co and NiO, after adequate magnetic field heat treatments. The hardening of the FM phase is optimized by varying the AFM:FM ratio.

EXPERIMENTAL

Different AFM:FM weight ratios (0:1, 3:7, 2:3, 1:1 and 3:2) of gas - atomized powders of NiO (99%, $<100 \mu\text{m}$, $T_N = 590 \text{ K}$) and Co (99.5%, $<44 \mu\text{m}$, $T_C = 1404 \text{ K}$) were mixed and sealed under Ar atmosphere in an agate vial ($V = 20 \text{ ml}$), together with 6 agate balls (10 mm diameter), with a ball to powder weight ratio of 2:1. The milling was carried out for different

times (0.1-30 hours), at 500 rpm, using a planetary mill. To induce exchange coupling, the as milled powders were annealed at different temperatures, $T_{ANN} = 300 - 850$ K, for different times (0-5 hours) under vacuum, in the presence of different magnetic fields (0 - 10 kOe), and field cooled to room temperature.

The microstructure of the powders was studied using standard x-ray diffraction (XRD) ($\text{Cu-K}\alpha$ radiation). The x-ray diffraction peaks were deconvoluted and fitted using a pseudo-Voigt function. The crystallite size, $\langle D \rangle$, was evaluated using a single peak method from its integral breadth (Cauchy component), following Scherrer's approximation. 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).

RESULTS AND DISCUSSION

Shown in fig. 1(a) is a SEM image (secondary electron) for the NiO-Co powders ball milled for 20 hours in a weight ratio of 1:1. Ball milling induces a broad range of particle sizes, from 1 μm to 30 μm [11]. The larger particles (an enlargement of one of these particles is shown in fig. 1) are composed of about 1 μm thick lamellae, surrounded by small particles. As can be seen in fig. 1(b) the Co x-ray mapping indicates that the lamellae (bright in fig. 1(a)) correspond to Co while the particles (gray in fig. 1(a)) correspond to NiO. This microstructure, typical of ball milled ceramic-metal mixtures, is due to the ductile and brittle character of Co and NiO respectively. Moreover, this microstructure allows the existence of a large interface area between the FM and the AFM phases.

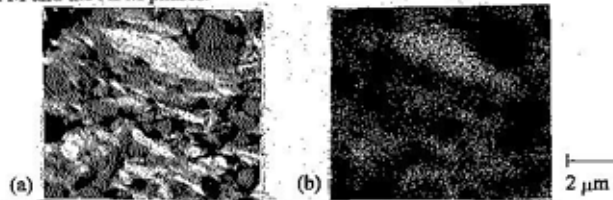


Fig. 1 (a) SEM secondary electron image and (b) Co EDX mapping for a (NiO)1:1(Co) ball milled for 20 h.

X-ray diffraction (XRD) patterns have been obtained for the unmilled Co and NiO and for the 20 h ball milled NiO-Co in a weight ratio of 1:1, before and after field annealing them in a 5 kOe magnetic field at $T_{ANN} = 600$ K. The XRD patterns of the unmilled Co reveal that it corresponds to a mixture of hcp and fcc Co, while the unmilled NiO powder diffraction peaks correspond to a fcc phase. The crystallite sizes, evaluated for the Co hexagonal (002) and the NiO (111) peaks, are $\langle D \rangle_{\text{Co,Hex}} = 42 \pm 4$ nm and $\langle D \rangle_{\text{NiO}} > 100$ nm, respectively [11].

When Co and NiO powders are ball milled together in a 1:1 weight ratio the intensity of the peaks corresponding to the fcc Co phase rapidly decreases. This allotropic transformation has been previously reported for ball milled Co powders [12]. The peak widths of the different phases after ball milling show an important increase. This is related to the crystallite size reduction, the introduction of planar defects and the microstrain increase. The crystallite sizes, after 20 hours of milling, estimated from the (002)_{Co,Hex} and the (111)_{NiO} reflections, are: $\langle D \rangle_{\text{Co,Hex}} = 10 \pm 2$ nm and $\langle D \rangle_{\text{NiO}} = 14 \pm 2$ nm, respectively. In addition, the positions of the

NiO peaks do not change after ball-milling, indicating no important variation in its lattice parameter. This suggests that the diffusion of Co into the NiO cell is very small [11].

When the ball milled NiO-Co powders are annealed at $T_{ANN} = 600$ K for 0.5 hours the x-ray diffraction pattern is very similar to that of the as milled powders, where the NiO peaks are not displaced and only a minor decrease in the peak width is obtained. The crystallite size calculated from the (111)_{NiO} reflection is $\langle D \rangle_{NiO} = 18 \pm 2$ nm. The Co-hcp phase shows a similar behavior, with $\langle D \rangle_{Co(hcp)} = 18 \pm 2$ nm, calculated from the (002)_{Co(hcp)} peak. Moreover, at this annealing temperature, a slight increase in the intensity of the (200)_{Co(fcc)} peak can already be observed, indicating the starting point for an allotropic transformation from hcp to hcp+fcc [12]. However, after annealing at $T_{ANN} = 740$ K for 0.5 hours, the crystallite sizes, calculated from (100)_{Co(fcc)} and (111)_{NiO} peaks, increase significantly to $\langle D \rangle_{Co(fcc)} = 44 \pm 4$ nm and $\langle D \rangle_{NiO} = 40 \pm 4$ nm and the intensity of the peaks corresponding to the cubic phase increases. Thus, annealing at $T_{ANN} = 740$ K induces an important crystal growth and the allotropic phase transformation from hcp to fcc Co [11].

The room-temperature coercivity, H_c , has been measured as a function of the milling time for the different NiO:Co weight ratios for both as-milled and annealed ($T_{ANN} = 600$ K) powders. In pure Co, H_c increases after a short milling time (1 hour) from $H_c = 170$ Oe (as obtained) to 290 Oe (1 hour ball milled) [13]. This increase is attributed to the allotropic phase transformation from fcc+hcp Co to hcp Co, where hcp Co is known to have larger H_c than fcc Co [14]. Further milling decreases H_c (e.g. $H_c = 125$ Oe after milling 30 hours), which is probably linked with the disordering of the hexagonal structure, as has been reported for long-term milling [12]. A maximum in H_c is also observed for ball milled NiO:Co. However, for each AFM:FM ratio, the largest H_c is obtained for different milling times, which increase as the NiO content increases, indicating that NiO probably delays the Co structural changes.

Annealing the ball milled pure Co powders at $T_{ANN} = 600$ K (i.e. $T_N < T_{ANN} < T_C$) for 0.5 hours in $H = 5$ kOe results in a slight decrease in H_c . However, a significant enhancement of H_c is observed after annealing the ball milled NiO-Co powders at the same temperature, $T_{ANN} = 600$ K, and field cooling ($H = 5$ kOe) to room temperature [13]. Shown in fig. 2 is the dependence of the coercivity enhancement (defined as the difference of H_c after and before annealing at T_{ANN} , ΔH_c) on the annealing temperature for (NiO):1:(Co) ball milled 20 h. As can be seen in the figure, the room-temperature H_c increases only when the annealing temperature is larger than the NiO Néel temperature (i.e. $T_N = 590$ K), as expected for an exchange coupled FM-AFM system [9]. The decrease of ΔH_c after annealing at exceedingly high temperatures ($T_{ANN} > 700$ K) is due to the allotropic phase transformation from fcc+hcp Co to fcc Co, as

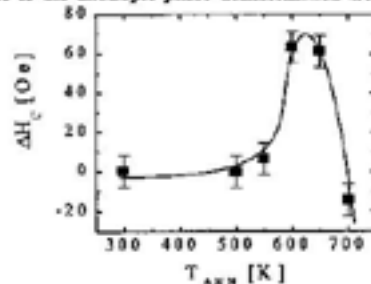


Fig. 2 Dependence of the coercivity enhancement, ΔH_c , on the annealing temperature for a (NiO):1:(Co) ball milled for 20 h.

observed from XRD. Loop shifts in the field axis, H_E , towards the negative field axis are also present in the hysteresis loops of the ball milled NiO-Co samples for all AFM:FM ratios, except in pure Co. The loop shifts depend on the annealing temperature with a similar dependence as ΔH_C , confirming the assumption that the exchange coupling between the AFM and the FM is responsible for both effects, ΔH_C and H_E .

Exchange coupling produces not only an enhancement of H_C but also an enhancement of the squareness, M_R/M_S [13], and consequently an increase of the energy product, BH_{Max} . The dependence of H_E , ΔH_C and ΔBH_{Max} (defined as the difference of BH_{Max} after and before annealing at $T_{ANN} = 600$ K) on the Co content (NiO:Co ratio) is shown in fig. 3. The values shown in the figure correspond to the milling times which give the maximum values of H_C for each NiO:Co ratio. As can be seen in the figure, the largest exchange coupling effects, i.e. maximum enhancements of H_C and BH_{Max} and maximum loop shifts, are exhibited for the (NiO)1:1(Co) ratio. However, the maximum value of BH_{Max} after annealing at $T_{ANN} = 600$ K is not obtained for (NiO)1:1(Co) ($BH_{Max} = 62000$ G.Oe) but for (NiO)2:3(Co) ($BH_{Max} = 83000$ G.Oe). This is due to the interplay between H_C and M_S on BH_{Max} . The addition of an AFM and the subsequent heat treatments increase H_C , however the AFM also promotes a reduction in the overall M_S of the composite. Hence, the enhancement of BH_{Max} is a compromise between both effects.

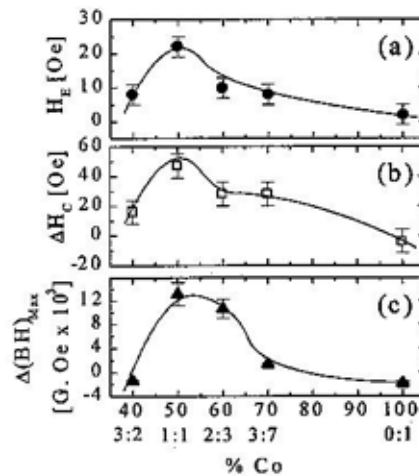


Fig. 3 Dependence of the (a) exchange bias, H_E , (b) coercivity enhancement, ΔH_C , and (c) enhancement of the energy product, $\Delta(BH)_{Max}$, on the Co percentage (NiO:Co ratio).

Shown in fig. 4 is the dependence of the loop shift on the measuring temperature. As expected from exchange coupled AFM-FM systems, H_E decreases as measuring temperature increases, becoming zero at $T \approx 600$ K, i.e. at the Néel temperature of the AFM (T_N (NiO) = 590 K). A similar behavior is observed for ΔH_C and $\Delta(BH)_{Max}$. The decrease of these properties with increasing measuring temperature is the result of a reduction of the AFM/FM interface coupling,

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 completely vanish is usually denoted as the blocking temperature, T_B [9].

To study the thermal stability of the ball milled NiO:Co systems due to the concomitant distribution of blocking temperatures [15] (brought about by the distribution of crystallite sizes and defects), the NiO:Co samples were warmed to a temperature T_D , $300 \text{ K} < T_D < 700 \text{ K}$, and subsequently cooled to room temperature in a field $H = -5 \text{ kOe}$, i.e. opposite to the one used to induce the original coupling ($H = 5 \text{ kOe}$).

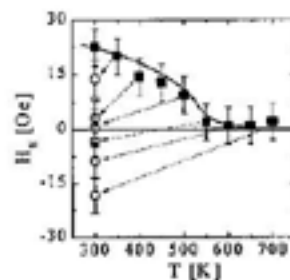


Fig. 4 Temperature dependence of the exchange bias, H_E ($^{\circ}$), on the measuring temperature, and H_E ($^{\circ}$) after field cooling in $H = -5 \text{ kOe}$ from different temperatures.

Following this procedure, if the local blocking temperature of a crystallite (T_B) is below T_D , the crystallite becomes paramagnetic, thus losing the information of the original coupling. Cooling such crystallite in $H = -5 \text{ kOe}$ induces a coupling opposite to the original one, hence shifting the loop towards positive fields. However, crystallites with $T_B > T_D$ remain unchanged. Consequently, the H_E obtained after warming to each T_D gives a measure of the number of crystallites with $T_B < T_D$ [15]. As can be seen in fig. 4, already at $T_D = 350 \text{ K}$ a reduction in H_E can be observed. Moreover, for $T_D = 500 \text{ K}$ H_E is reduced to zero (i.e. 50 % of the crystallites have $T_B < 500 \text{ K}$). These results indicate a broad distribution of blocking temperatures in this system. However, although the thermal stability of H_E is strongly influenced by the distribution of T_B , we observed that H_C is rather insensitive to it. This is probably because although the overall H_E depends on the strength and sign of the coupling for each crystallite, the enhancement of H_C depends only on the strength of the coupling.

CONCLUSIONS

In conclusion, we have shown that mechanically milled AFM(NiO) - FM(Co) composites display significant enhancements of the room temperature coercivity and energy product due to the exchange coupling induced after heat treating the samples at $T_{heat} > T_B$ under magnetic fields. The as-milled powders exhibit a peculiar microstructure (Co lamellae surrounded by refined NiO particles), which allows the existence of a large interface area between the FM and the AFM. The maximum magnetic hardening is shown to be a trade off between the coercivity enhancement produced by exchange coupling and the overall reduction of saturation magnetization due to the antiferromagnet. All the effects (H_C , H_E and BH_{max}) decrease with increasing temperature and the NiO-Co samples become uncoupled when the

measuring temperature is larger than the antiferromagnetic Néel temperature. Although H_E is strongly influenced by the distribution of T_D , H_C remains rather insensitive to it.

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