

Article III

Correlation between the Microstructure and Enhanced Room Temperature Coercivity in Ball Milled Ferromagnetic - Antiferromagnetic Composites

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Abstract

Ball milling a metallic ferromagnet (Co) with an oxide antiferromagnet (NiO) produces a microstructure consisting of ferromagnetic lamellae separated by antiferromagnetic particles. Due to its large antiferromagnetic - ferromagnetic interface this microstructure induces an exchange interaction when the samples are field cooled from above the antiferromagnetic Néel temperature. This interface exchange interaction results in a substantial enhancement of the room temperature coercivity of the ferromagnetic phase.

Introduction

Synthesis of composite materials, such as metal-ceramics, has been found to induce a range of interesting properties including high temperature strength, high wear resistance, high melting points and good corrosion and oxidation resistance [1-3]. Mechanical milling [4] is a low cost method for the production of these materials. Moreover, at the early stages of milling, metallic - ceramic composites exhibit a peculiar microstructure, composed of metal lamellae separated by elongated ceramic particles [5]. Mechanical alloying has also been used to produce direct or indirect magnetic interactions, like in exchange spring magnets [6,7] or giant magnetoresistance materials [8].

In this paper we exploit the special microstructure of the metal-ceramic composites to induce exchange interactions between a metallic ferromagnet (FM), Co, and an oxide antiferromagnet (AFM), NiO. This interaction brings about an increase of the coercivity, H_C , of the ferromagnetic phase when the samples are warmed to above the AFM (NiO) Néel temperature, T_N , and field cooled to room temperature. This enhancement of H_C is caused by the exchange coupling at the AFM - FM interface.

Experimental

Gas - atomized powders of Co (99.5%, $< 44 \mu\text{m}$, $T_C = 1404 \text{ K}$) and NiO (99%, $< 100 \mu\text{m}$, $T_N = 590 \text{ K}$), were mixed in 1:1 weight ratio 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 (Fritsch Pulverisette 7). For comparison, ball milling of pure Co was also carried out under the same conditions. The as milled powders were annealed at different temperatures $T_{ANN} = 300 - 850 \text{ K}$ for different times (0-5 hours) in 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) (Cu-K α radiation). Their morphological characterization was performed by using scanning electron microscopy (SEM), equipped with energy dispersive x-ray analysis (EDX). The x-ray diffraction peaks have been deconvoluted and fitted using a pseudo-Voigt function. The crystallite size, $\langle D \rangle$, has been evaluated using a single peak method from its integral breadth (Cauchy component), following Scherrer's approximation [9]. In order to perform the SEM observations, the Co-NiO powders were mounted in an epoxy resin and subsequently polished. Magnetic hysteresis loops, up to 10 kOe, were carried out in loosely packed powders, at room temperature, by means of vibrating sample magnetometry (VSM).

Results

i) Structural

The SEM image (secondary electron) for the NiO and Co powders ball milled for 20 hours is shown in figure 1. As can be observed in the figure, ball milling induces a broad range of particle sizes, from 1 μm to 30 μm . The larger particles show a Co (ductile) lamellar microstructure, about 1 μm thick, separated by NiO particles (brittle). Note that the composition of the lamellae and the particles was confirmed from the EDX analysis.

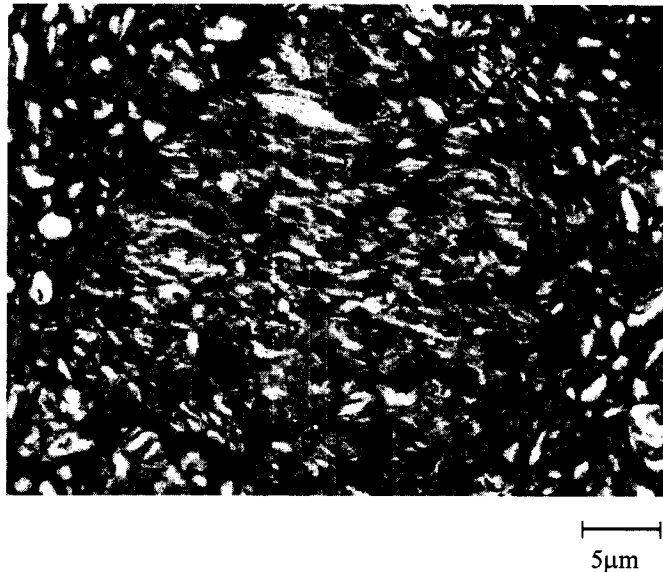


Fig 1: Secondary electrons, SEM image of the Co-NiO 1:1 ball-milled for 20 hours, where the white, gray and black correspond to Co, NiO and resin, respectively.

The XRD patterns of the unmilled Co and NiO and the Co+NiO ball milled for 20 hours, are shown in figure 2. The unmilled Co powders show reflections corresponding to hcp and fcc phases, while the unmilled NiO powder shows peaks corresponding to a fcc phase. The crystallite size can be evaluated for the Co-hcp phase considering non faulted reflections, $h - k \neq 3n \pm 1$ (h and k are the Miller indexes of the hcp phase, and n is an integer). Note that for Co, the reflections with $h - k$

$= 3n \pm 1$, are more sensitive to deformations or growth faults [10,11]. For this reason the crystallite size has been evaluated for the $(002)_H$ peak (which has been deconvoluted from the $(111)_C$ peak) giving $\langle D \rangle_{Co,H} = 42$ nm. The crystallite size for the NiO phase, $\langle D \rangle_{NiO}$, is larger than 100 nm.

When the Co powders are ball milled with NiO powders the intensity of the peaks corresponding to the fcc Co phase rapidly decreases. For example, after 20 hours of milling, the $(200)_C$ reflection is only observable as a small shoulder, close to the $(101)_H$ peak (figure 2). This allotropic transformation has been previously reported for ball milled Co powders [10,12]. In addition, the position of the NiO peaks does 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 small. However, EDX analyses reveal a certain degree of Co-Ni diffusion. 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 $(002)_H$ and $(111)_{NiO}$ reflections, are: $\langle D \rangle_{Co,H} = 10$ nm and $\langle D \rangle_{NiO} = 14$ nm, respectively.

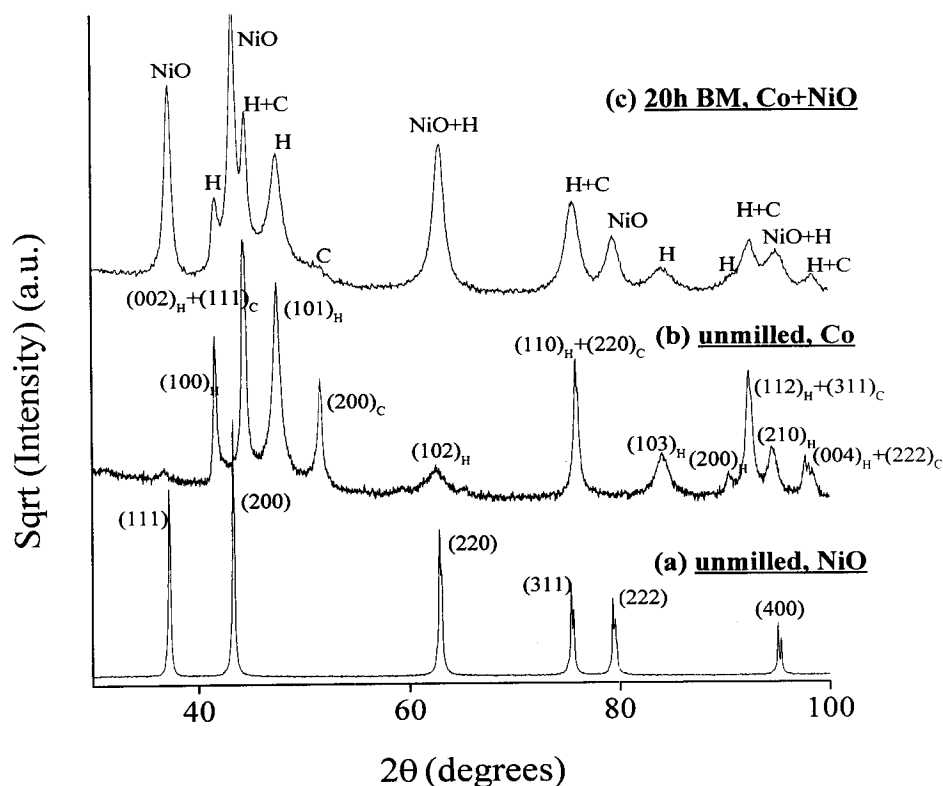


Fig 2: X-ray diffractograms for (a) unmilled NiO, (b) unmilled Co and (c) Co + NiO ball milled for 20 hours. Note that the curves have been shifted for clarity.

In figure 3 it can be observed that when the ball milled powders are heat-treated at $T_{ANN} = 600$ K for 0.5 hours the NiO peaks show no displacement, but a small decrease in the peak width. The crystallite size calculated from the $(111)_{NiO}$ reflection is $\langle D \rangle_{NiO} = 18$ nm. The Co-hcp phase

shows a similar behavior, with $\langle D \rangle_{\text{Co,H}} = 18$ nm, calculated from $(002)_{\text{H}}$. Moreover, at this temperature, a slight increase in the intensity of the $(200)_{\text{C}}$ peak can already be observed, indicating the starting point for an allotropic transformation from hcp to hcp+fcc [10]. After annealing at $T_{\text{ANN}} = 740$ K for 0.5 hours the crystallite sizes, calculated from $(100)_{\text{H}}$ and $(111)_{\text{NiO}}$ peaks, increase to $\langle D \rangle_{\text{Co,H}} = 44$ nm and $\langle D \rangle_{\text{NiO}} = 40$ nm, respectively. Thus, annealing at $T_{\text{ANN}} = 740$ K induces an important crystal growth. Moreover, the $(200)_{\text{C}}$ peak is clearly visible, thus the hcp to hcp + fcc allotropic transformation is taking place (figure 3).

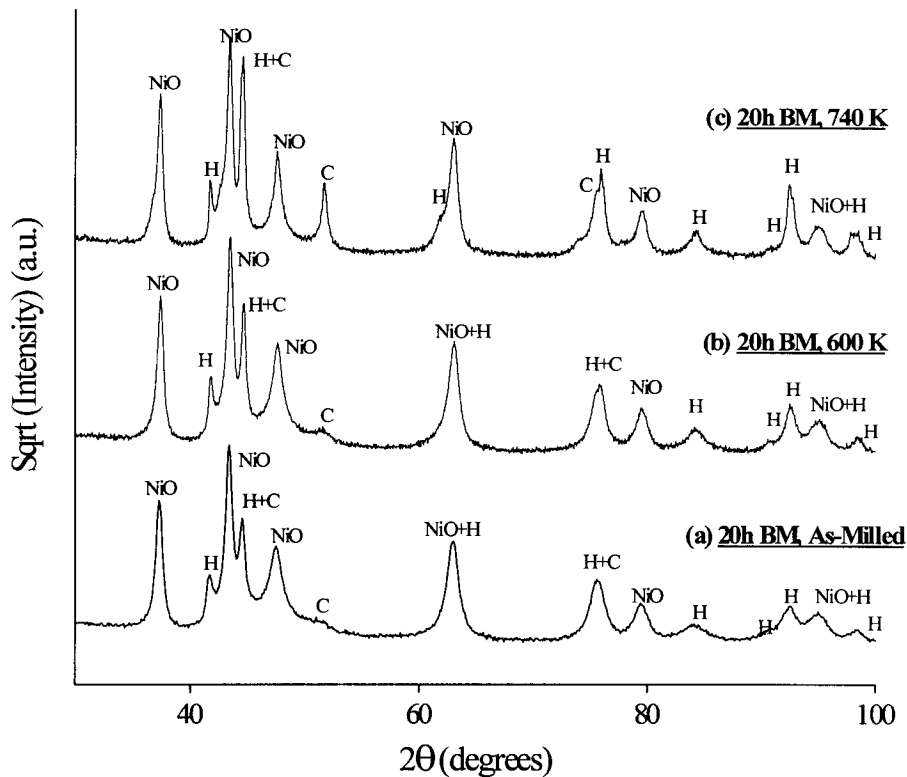


Fig 3: X-ray diffractograms for Co + NiO 1:1 ball milled for 20 hours, (a) as milled, (b) annealed at $T_{\text{ANN}} = 600$ K for 0.5 hours and (c) $T_{\text{ANN}} = 740$ K for 0.5 hours. Note that the curves have been shifted for clarity.

ii) Magnetic

The coercivity, H_{C} , for the pure Co powders increases after a short milling time (1 hour), from $H_{\text{C}} = 170$ Oe (as obtained) up to $H_{\text{C}} = 290$ Oe (1 hour ball milled). Further milling decreases H_{C} (e.g. $H_{\text{C}} = 125$ Oe after milling 30 hours). A maximum in H_{C} is also observed for ball milled Co-NiO particles when increasing the milling time. However, the presence of NiO delays the appearance of the maximum to 20 hours of milling [13]. Annealing the ball milled pure Co powders at $T_{\text{ANN}} = 600$ K for 0.5 hours in $H = 5$ kOe produces virtually no change in H_{C} . However, annealing the ball milled Co-NiO powders at $T_{\text{ANN}} = 600$ K for 0.5 hours in $H = 5$ kOe induces a significant increase in H_{C} , for milling times longer than 10 hours. The dependence of H_{C} on the

annealing temperature, T_{ANN} , for different milling times, is shown in figure 4. The maximum H_C is always obtained for $T_{ANN} = 600$ K, i.e. for $T_{ANN} > T_N = 590$ K. Note that small loop shifts, towards negative fields, are also present in the hysteresis loops of the ball milled Co-NiO samples. The maximum enhancement of H_C occurs when the samples are milled for 20 hours. In this case a loop shift of about 25 Oe is observed after annealing at 600 K for 0.5 hours under a field of $H = 5$ kOe [13].

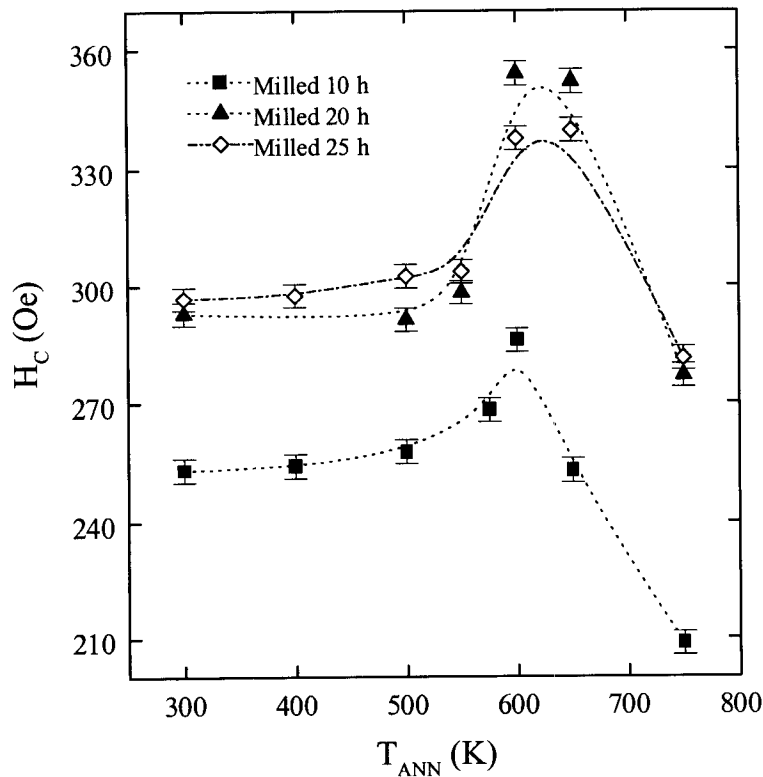


Fig 4: Dependence of the coercivity, H_C , on the annealing temperature, T_{ANN} , for Co-NiO 1:1 powders milled for 10 hours (-■-), 20 hours (-▲-) and 25 hours (-◇-) and annealed during 0.5 hours at $H = 5$ kOe. The lines are a guide to the eye.

Annealing time is found to play also an important role. Long annealing times (several hours) tend to slowly transform hcp-Co towards fcc-Co, leading to a decrease of the H_C enhancement. A maximum coercivity of around 370 Oe was achieved after annealing 3 hours at $T_{ANN} = 600$ K in $H = 5$ kOe, for the sample ball milled 20 hours.

Discussion

The enhanced H_C and the presence of loop shifts of the mechanically milled Co-NiO powders when annealing at temperatures above the Néel temperature of NiO indicate that it is the exchange interaction (exchange bias) between the AFM and the FM powders which induces the coercivity enhancement [14]. According to exchange bias, the increased coercivity and shifted loops should only appear when field cooling from above T_N [14]. That would indicate that an enhancement of H_C should be observed for any $T_{ANN} > T_N$. However, the observed decrease in H_C for high annealing temperatures is due to the transformation from hcp-Co to fcc-Co. Similar effects (increased coercivity and/or loop shifts) have been observed at low temperatures in Co particles embedded in their antiferromagnetic native oxide [15,16] and at room temperature in samples obtained by mechanical milling transition metals (Co, Ni and Fe) and their antiferromagnetic oxides (CoO or NiO) or sulfides (FeS) [17].

The microstructure of the ball milled powders helps to better understand the magnetic properties of the FM-AFM system. As the milling time increases, the thickness of the ductile lamellae (Co) is continuously refined while the ceramic particles (NiO) are broken up into fine pieces, thus increasing the AFM - FM interface area. This increase of interface area induces an increased coupling between the AFM and FM phases when the samples are field cooled from above T_N . In particular, exchange coupling effects have been found to depend on structural defects in the AFM [18]. Thus, one would expect an increase on the enhancement of H_C for increasing milling times, as observed up to 20 hours of milling. This result would be in agreement with the decrease of the $\langle D \rangle_{NiO}$ (i.e. introduction of structural defects). The decrease of H_C for longer milling times may be due to excessive defects in Co (as indicated from the x-ray analysis) or that Co and NiO are starting to alloy (as indicated by EDX analysis). In order to study the effect of the morphology in the magnetic properties, the 20 hours milled Co-NiO particles were separated into different sizes, Φ , by using different sieves. Note that the large particles exhibit a large number of interfaces, while smaller particles have few or no FM-AFM interfaces (see Fig. 1). As expected, the coercivity of as milled powders of different sizes is similar except for the smallest particles (Table I), because before field cooling there should be no coupling present. After annealing at $T_{ANN} = 600$ K for 0.5 hours in $H = 5$ kOe, the samples were found to depend markedly on Φ . The highest values of H_C were obtained for $\Phi > 50 \mu\text{m}$, as expected from their microstructure (i.e. maximum interface area).

Particle Size (μm)	$\Phi > 100$	$50 < \Phi < 100$	$25 < \Phi < 50$	$\Phi < 25$
H_C (Oe), as milled	303 ± 3	306 ± 3	301 ± 3	291 ± 3
H_C (Oe), annealed	353 ± 3	355 ± 3	343 ± 3	330 ± 3

Table I. Coercivity, H_C , for particles of different sizes of Co-NiO 1:1 samples ball milled for 20 hours and annealed for 0.5 hours at $T_{ANN} = 600$ K in $H = 5$ kOe

Conclusion

In conclusion, we have shown it is possible to enhance the room temperature coercivity of Co powders by milling them with an oxide AFM with T_N above room temperature, such as NiO. This enhancement is caused by the exchange interaction (exchange bias) at the AFM - FM interface after field cooling from above the AFM T_N . The microstructure of lamellae of the ductile metallic FM (Co) separated by particles of the brittle oxide AFM (NiO) is found to be effective in inducing the necessary interface coupling for coercivity enhancement.

Acknowledgements

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