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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.* [S0003-6951(99)05246-8]

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
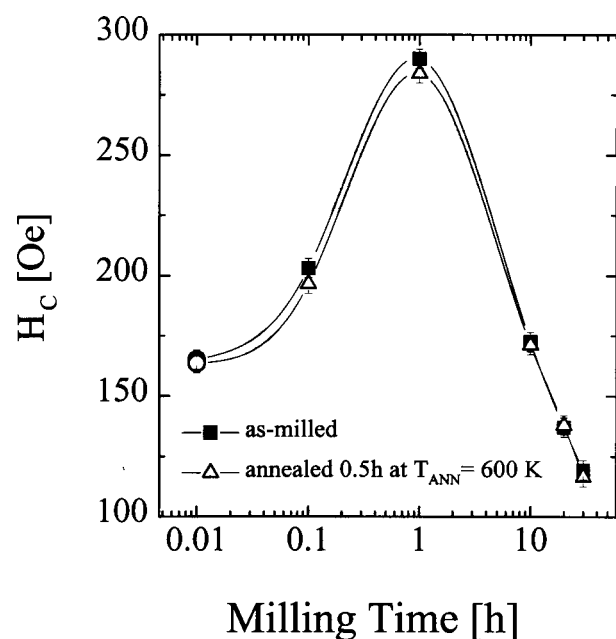

FIG. 1. Dependence of the coercivity, H_C, on the milling time for Co powders for as milled (full symbols) and milled and annealed at $T_{ANN}=600$ K for 0.5 h at $H=5$ kOe (open symbols). Note that the circles are for the original Co powders, as-obtained (full symbol) and annealed at $T_{ANN}=600$ K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

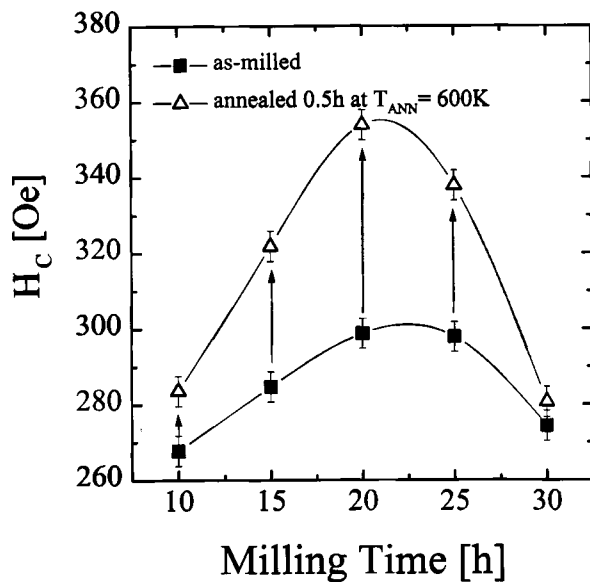[a]Electronic mail: Dolors.Baro@UAB.ES

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)
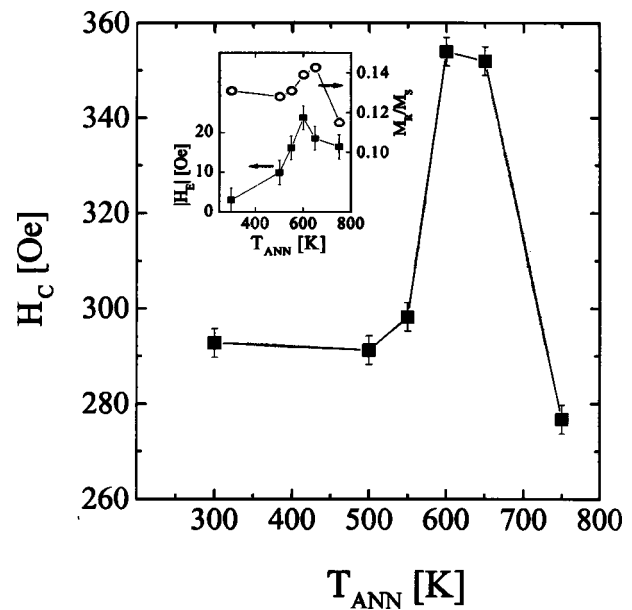
tend to either slowly transform hcp-Co towards fcc-Co and/or probably induce excessive interdiffusion, leading to a decrease of the H_C enhancement. In our case, for the sample mechanically alloyed for 20 h annealing for more than 3 h was found to deteriorate the properties. The maximum coercivity increase 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,
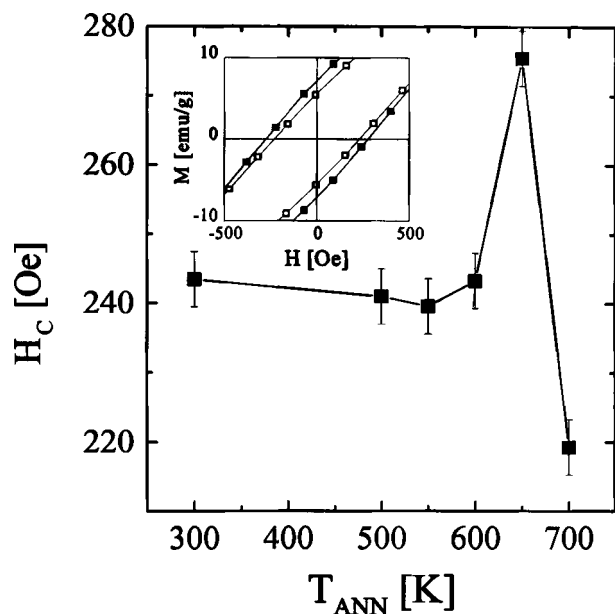
FIG. 4. Dependence of the coercivity, H_C, on the annealing temperature, T_{ANN}, for Co–FeS 1:1 powders milled for 10 h and annealed during 0.1 h at $H=5$ kOe. Shown in the inset are the hysteresis loops of the as-milled sample (open symbols), and the sample annealed at $T_{ANN}=650$ K for 0.1 h (full 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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