Coercivity and squareness enhancement in ball-milled hard magnetic–antiferromagnetic composites

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The room-temperature coercivity, $H_C$, and squareness, $M_R/M_S$ (remanence/saturation magnetizations), of permanent magnet, SmCo$_5$ powders have been enhanced by ball milling with antiferromagnetic NiO (with Néel temperature, $T_N=590$ K). This enhancement is observed in the as-milled state. However, when the milling of SmCo$_5$ is carried out with an antiferromagnet with $T_N$ below room temperature (e.g., for CoO, $T_N=290$ K), the coercivity enhancement is only observed at low temperatures after field cooling through $T_N$. The ferromagnetic–antiferromagnetic exchange coupling induced either by local heating during milling (SmCo$_5$+NiO) or field cooling (SmCo$_5$+CoO) is shown to be the origin of the $H_C$ increase. © 2001 American Institute of Physics. [DOI: 10.1063/1.1392308]

During the last few decades permanent magnet development has been centered on the production of highly anisotropic materials and nanocomposite magnets consisting of a mixture of exchange coupled hard and soft magnetic components, commonly known as spring magnets. In the latter, a reduction of coercivity, $H_C$, cannot be avoided. Conversely, an enhancement of $H_C$ and a shift of the hysteresis loops along the field axis (exchange bias) are well known effects of antiferromagnetic (AFM)–FM exchange coupling. Exchange bias has been extensively studied in thin films, because of its role in spin-valve devices. However, the coercivity enhancement associated with exchange bias has been investigated less. In the case of powders, usually a widening of the loop is observed far below room temperature (RT), either because the Néel temperature, $T_N$, of the AFM is below RT or the AFM grains are so small that they behave superparamagnetically at RT. Exchange bias has been extensively studied in thin films, because of its role in spin-valve devices. However, the coercivity enhancement associated with exchange bias has been investigated less. In the case of powders, usually a widening of the loop is observed far below room temperature (RT), either because the Néel temperature, $T_N$, of the AFM is below RT or the AFM grains are so small that they behave superparamagnetically at RT.

The milling was carried out for different times (0.25–32 h) using a planetary mill.

The microstructure of the as-milled powders was studied by x-ray diffraction (XRD). XRD patterns were fitted using the Rietveld method from which the crystal lattice size, $D$, was evaluated for each component. Morphological characterization was performed using a scanning electron microscope (SEM). Magnetic hysteresis loops of tightly packed isotropic powders were carried out at RT with a maximum field of $\mu_0H_{\text{max}}=23$ T, by means of an extraction magnetometer. Hysteresis loops after zero-field cooling (ZFC) and field cooling ($\mu_0H_{\text{FC}}=5$ T) of SmCo$_5$ and SmCo$_5$+CoO were also carried out at $T=30$ and 100 K.

For the three systems studied (SmCo$_5$, SmCo$_5$+NiO and SmCo$_5$+CoO) the SmCo$_5$ crystal lattice size, $D$, is a decreasing function of the milling time, especially during the first 4 h of milling. However, this reduction is somewhat steeper when milling SmCo$_5$ alone. For long milling times the crystal lattice size stabilizes to a nanometric range (e.g., $D=10$ nm in SmCo$_5$+CoO), but $D$ remains larger in SmCo$_5$+CoO and SmCo$_5$+NiO than in SmCo$_5$ alone.

SEM micrographs of ball-milled SmCo$_5$ also reveal a reduction of the particle size and changes in shape with an increase in the milling time, from about 500 $\mu$m irregular and sharp-edged particles to roughly spherical particles of about 5 $\mu$m in the 32 h ball-milled SmCo$_5$. A different microstructure is encountered in ball-milled SmCo$_5$+NiO and SmCo$_5$+CoO. In both cases, in addition to the SmCo$_5$ particle size reduction, observed in SmCo$_5$ alone, the SmCo$_5$ particles in SmCo$_5$+AFM become progressively surrounded and soldered to NiO or CoO. After 32 h of milling they form aggregates of up to 10 $\mu$m in size composed of several SmCo$_5$ particles embedded in a NiO or CoO "matrix."

Shown in Fig. 1 is the milling time dependence of the coercivity, $H_C$, for the three series of powders, measured at RT. SmCo$_5$ exhibits typical behavior with milling time, i.e., a sharp increase of $H_C$ for short milling times, a maximum in $H_C$ ($\mu_0H_{\text{FC}}=1.1$ T after 4 h of milling), followed by a gradual decrease of $H_C$ for long milling times. Although
Note that small shifts, further in the SmCo$_5$ systems is similar, the low temperature coercivity increases SmCo$_5$ alone, the cooling to RT were also carried out for the SmCo$_5$. However, they resulted in a significant reduction of even from the early stages of milling an enhancement of the behavior of the three systems is similar for short milling times. It is also worth noting that $H_C$ is obtained in ball-milled SmCo$_5$+NiO in comparison with $H_C$ values of ball-milled SmCo$_5$ and SmCo$_5$+CoO.

As shown in Fig. 2, the coercivities of SmCo$_5$ (milled 4 h) and SmCo$_5$+CoO (milled 32 h) are both found to increase at low temperatures. Note that milling times exhibiting maximum RT $H_C$ were chosen for each system for the field cooling experiments. However, although the RT $H_C$ of both systems is similar, the low temperature coercivity increases further in the SmCo$_5$+CoO system after field cooling ($\mu_0 H_{FC} = 5$ T) to below $T_N$ than in SmCo$_5$ alone. Moreover, if SmCo$_5$+CoO is ZFC to low temperatures, the coercivity obtained ($\mu_0 H_C = 2.02$ T at $T = 100$ K) is clearly smaller than the one after field cooling ($\mu_0 H_{FC} = 2.19$ T at $T = 100$ K). Heat treatments above the $T_N$ of NiO and subsequent field cooling to RT were also carried out for the SmCo$_5$+NiO. However, they resulted in a significant reduction of $H_C$. Note that small shifts, $H_E$, of the hysteresis loops in the field axis were often observed for both SmCo$_5$ and SmCo$_5$+CoO ($\mu_0 H_E \approx 0.05$ T at RT and $\mu_0 H_E \approx 0.1$ T at $T = 100$ K).

The milling time dependence of the coercivity, $\mu_0 H_C$ (measured at room temperature) for ball-milled SmCo$_5$ (■, SmCo$_5$+CoO 1:1 (△) and SmCo$_5$–NiO 1:1 (○) powders. The lines are a guide to the eye. The behavior of the three systems is similar for short milling times, a maximum value of $H_C$ is obtained for SmCo$_5$+NiO, $\mu_0 H_C = 1.5$ T. Moreover, in contrast to what is observed for SmCo$_5$ alone, the $H_C$ for SmCo$_5$+NiO and SmCo$_5$+CoO levels off for long milling times. It is also worth noting that even from the early stages of milling an enhancement of $H_C$ is observed in ball-milled SmCo$_5$+NiO in comparison with $H_C$ values of ball-milled SmCo$_5$ and SmCo$_5$+CoO.

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served for SmCo$_5$ alone. Nevertheless, as expected from the FM–AFM coupling, SmCo$_5$+CoO exhibits extra $H_C$ enhancement at low temperatures with respect to single SmCo$_5$ after the same field cooling procedure. Further proof of the effect of FM–AFM coupling comes from $H_C$ in SmCo$_5$+CoO after ZFC. Although the local field of the SmCo$_5$ particles can induce AFM–FM coupling to the CoO even after ZFC from a demagnetized state, only those SmCo$_5$ particles which are single domain will fully contribute to it. In a field cooling experiment ($\mu_0H_{FC}=5$ T) the total magnetic moment of nearly all SmCo$_5$ particle spins is aligned parallel to the applied field direction, thus all particles contribute to the coupling. Hence, one would expect smaller coupling and consequently reduced $H_C$ enhancement after ZFC, as is observed experimentally.

Unfortunately, field cooling SmCo$_5$+NiO from above $T_N$ of NiO does not result in enhancement of $H_C$ as would be expected from AFM–FM coupling. This is because of the rapid decrease of $H_C$ of SmCo$_5$ when submitted to moderate annealing temperatures, due to the segregation of softer phases (Sm$_2$Co$_7$ and Sm$_2$Co$_{17}$). In other words, the decrease of $H_C$ at $T=600$ K (before the field cooling procedure) is more important than the possible gain due AFM–FM coupling. Note that the local temperature reached during milling can be above the temperature at which soft phases segregate. Nevertheless, the duration of local heating (only effective for a few $\mu$s) is exceedingly short to allow diffusion to induce segregation. Hence, the negative effects of the temperature are not observed during milling.

The existence of loop shifts is usually linked to AFM–FM exchange coupling, which strengthens our argument. However, loop shifts have also been observed in SmCo$_5$ alone, which is usually related to interface spin-glass states due to milling induced surface disorder. Although the Stoner–Wohlfarth model for isotropic, single domain, noninteracting particles predicts a squareness of $M_R/M_S=0.5$, small particle hard magnets are known to usually exhibit rather large squareness, similar to the values for SmCo$_5$ shown in Fig. 3. These high $M_R/M_S$ values are due to short-range exchange interactions among SmCo$_5$ particles. Thus, isolating the SmCo$_5$ particles should result in a reduction of $M_R/M_S$, as observed for SmCo$_5$+CoO after short milling times. Since CoO is paramagnetic at RT, essentially its role is simply to separate the SmCo$_5$ particles. The crossover at moderate milling times between the $M_R/M_S$ of SmCo$_5$+CoO and SmCo$_5$ alone is probably due to the more aggressive effects of milling on SmCo$_5$ alone. Contrary to what is observed in ball-milled SmCo$_5$+CoO, in SmCo$_5$+NiO even higher $M_R/M_S$ values are obtained in comparison with ball-milled SmCo$_5$. Hence, the presence of the AFM NiO phase surrounding SmCo$_5$ seems to play an important role in further enhancing $M_R/M_S$. Despite the fact that $M_R/M_S$ enhancement has also been observed in other AFM–FM systems, its origin, although clearly related to AFM–FM interaction, is not well understood.

Finally, note that, although the effects described appear to be clearly linked to AFM–FM exchange interactions, some effects from the differences in microstructure and surface disorder cannot be completely ruled out.

In conclusion, we have shown that the coercivity and squareness of permanent magnet powders (e.g., SmCo$_5$) can be enhanced after milling them with an antiferromagnet. To obtain these enhancements at RT and above it is necessary to induce exchange coupling between the permanent magnet and an antiferromagnet with $T_N$>RT. Hence, this study opens up new possibilities for improvement of permanent magnet’s magnetic properties.

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11 SmCo$_5$ powders obtained from Alfa-Aesar.