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Richard L. Schalek

*University of Nebraska - Lincoln*

Diandra Leslie-Pelecky

*University of Nebraska - Lincoln*, diandra2@unl.edu

John Knight

*University of Nebraska - Lincoln*

David J. Sellmyer

*University of Nebraska-Lincoln*, dsellmyer@unl.edu

Steven C. Axtell

*University of Nebraska - Lincoln*

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## Tailoring of the Magnetic Properties of $\text{SmCo}_5\text{:Nb}_{0.33}\text{Cr}_{0.67}$ Nanocomposites Using Mechanical Alloying

Richard L. Schalek<sup>#</sup>, Diandra L. Leslie-Pelecky<sup>\*</sup>, John Knight<sup>#</sup>, D.J. Sellmyer<sup>\*</sup> and Steven C. Axtell<sup>#</sup>  
Center for Materials Research and Analysis, University of Nebraska, Lincoln, NE 68588-0113

**Abstract**—Nanocomposite structures composed of ferromagnetic particles dispersed in a matrix are systems in which the magnetic properties can be tailored by varying the size and spacing of the ferromagnetic particles. Nanocomposites of  $\text{SmCo}_5$  in a non-magnetic  $\text{Nb}_{0.33}\text{Cr}_{0.67}$  matrix exhibit a wide variety of magnetic properties.  $\text{SmCo}_5$  powder is premilled prior to mechanical alloying. The premilling results in a maximum coercivity of 16 kOe after 2 hours of milling, and an enhanced remanence ratio. Both features may be due to exchange anisotropy and/or exchange coupling between hard and soft ferromagnetic phases. The nanocomposite samples show that, when the  $\text{SmCo}_5$  particulates are small enough, the primary effect of alloying is to disperse them throughout the matrix with no further refinement of size.

### I. INTRODUCTION

Mechanical alloying is a powerful fabrication technique that provides the ability to tailor the nanostructure of materials. The intricate linkage between nanostructure and magnetism in turn allows tuning of the magnetic properties of the material to a desired set of specifications by varying the magnetic particle size and spacing between magnetic particles. The first of these parameters is varied by premilling the magnetic powder; the second, by varying the concentration of magnetic material in the finished product. Surface effects are enhanced by the large fraction of interfaces in mechanically alloyed systems.

The complex phase diagram of the Sm-Co system makes producing single-phase stoichiometric  $\text{SmCo}_5$  challenging without annealing subsequent to fabrication.[1,2] We chose to start by pre-milling commercially purchased crystalline  $\text{SmCo}_5$  powders (-100 mesh, 99.9% purity) in a SPEX 8000 mixer/mill with WC-lined vials and three 12 g-WC balls. All sample handling, including the milling, was done in an argon atmosphere to reduce oxidation. Throughout this paper, the term 'milling' is used to describe processing of the  $\text{SmCo}_5$  powder and 'alloying' is reserved for reference to the mixing of the  $\text{SmCo}_5$  powder and the matrix material.

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\* Also Department of Physics and Astronomy

# Also Department of Mechanical Engineering

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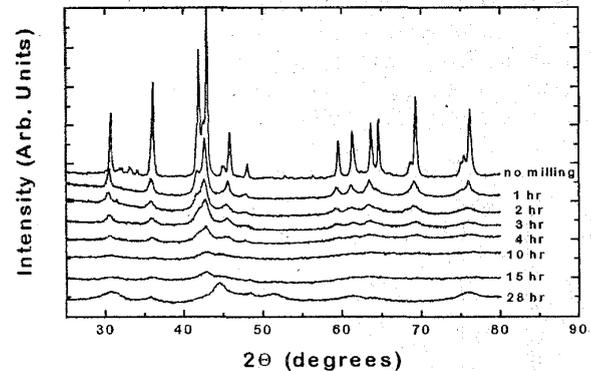


Fig. 1. The X-Ray diffraction spectra of premilled  $\text{SmCo}_5$ .

### II. PREMILLED $\text{SmCo}_5$

Prior to mechanically alloying with Nb and Cr, the  $\text{SmCo}_5$  was premilled to reduce the magnetic particle size. Premilling times ranged from 15 minutes to 30 hours. Fig. 1 indicates that the  $\text{SmCo}_5$  quickly becomes amorphous on the length scales probed by x-ray diffraction after minimal milling times. Peaks appearing for milling times greater than 15 hours may be indexed to the high-temperature, cubic phase of cobalt.

Diffraction crystallite size as a function of milling time (shown in Fig. 2) was obtained by a Fourier analysis that separates the broadening effects of strain from those due to particle size.[3] The diffracting crystallite size becomes too small for accurate estimation at milling times greater than 4 hours.

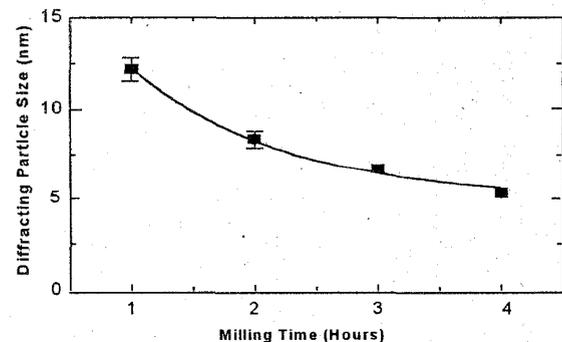


Fig. 2. Diffracting crystallite size of premilled  $\text{SmCo}_5$  as a function of milling time.

Milled powders were mixed with paraffin, packed in polyethylene bags and sealed in an argon atmosphere to reduce oxidation during magnetic measurements. The paraffin prevents magnetization reversal via rotation of the entire particle. Samples were measured in both unaligned and aligned configurations. For the aligned configuration, the paraffin was melted, a magnetic field of 55 kOe was applied and the sample cooled in the field to solidify the paraffin.

Hysteresis loops of premilled  $\text{SmCo}_5$  were studied as functions of premilling times to facilitate understanding of the effect of the nanocomposite structure relative to free nanoscale particles. Fig. 3 shows the coercivity,  $H_c$ , and remanence ratio,  $M_r/M_s$ , for premilled  $\text{SmCo}_5$  as a function of milling time. Error bars (omitted for clarity) are smaller than the symbol size. Open symbols represent samples measured in an unaligned state while solid symbols represent measurements of aligned powders.  $H_c$  rises rapidly with milling time, increasing by a factor of three after just 15 minutes of milling. The maximum coercivity of 16 kOe is achieved after 2 hours of milling. This corresponds to a diffracting crystallite size of about 6 nm. Coincident with the rapid increase in  $H_c$  is a decrease in the remanence ratio from a high of 0.90 to approximately 0.70.  $H_c$  does not significantly depend on whether the samples are measured in the aligned or unaligned states for the milled samples. The remanence shows a slight dependence on alignment, but is enhanced in both aligned and unaligned states for milling times up to 18 hours. In contrast, the remanence for aligned unmilled powders is much higher (0.80) than for unaligned unmilled powders (0.50).

As shown in Fig. 3, three regimes are identifiable as a function of milling time. In the first (0-2 hours),  $H_c$  increases and  $M_r/M_s$  decreases. In the second (2-16 hours),

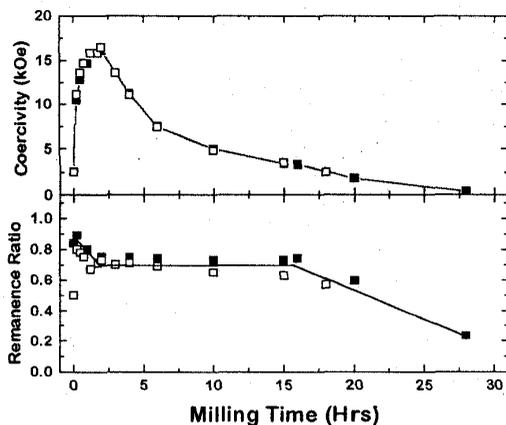


Fig 3: The remanence and coercivity as a function of milling time for  $\text{SmCo}_5$  powders. Open symbols represent powders measured in the unaligned state, while solid symbols represent powders measured in an aligned state.

$H_c$  decreases while  $M_r/M_s$  remains relatively flat, and in the third,  $H_c$  continues a slow decrease and  $M_r/M_s$  exhibits a near linear decay.

The behavior of the premilled  $\text{SmCo}$  is complicated, but two likely mechanisms may be identified. (1) The hysteresis loops are shifted toward negative values on the magnetic field axis, with the magnitude of the shift exhibiting the same dependence on milling time as the coercivity. This shift is a signature of exchange anisotropy, usually due to the proximity of antiferromagnetic and ferromagnetic regions.[4] Although the material was handled carefully to avoid oxidation, there is the likelihood that a thin layer of surface oxidation (possibly  $\text{CoO}$ ) is present. The magnitude of the coercivities in these materials suggests that the oxidation is limited to the surface and that significant regions of ferromagnetic  $\text{SmCo}_5$  are present. The larger number of interfaces in mechanically milled materials may increase the effect of exchange coupling. Although we might expect this system to be similar to the  $\text{Co/CoO}$  system, the temperature dependence of the shift does not agree with the numerical forms reported in the literature. A shift upward on the positive magnetization axis is also observed at low temperatures.

(2) The hysteresis loop displays a large reversible component for fields less than the coercive field. This behavior is also seen in 'exchange-spring' magnets due to exchange coupling of regions of hard and soft ferromagnetic material[5]. X-Ray diffraction scans of samples milled for longer times indicate the presence of cubic  $\text{Co}$ . Smaller quantities of  $\text{Co}$  may be present at shorter milling times that would produce the hard/soft ferromagnetic regions necessary for exchange coupling. Exchange coupling would also explain the enhanced remanence at room temperature. Again, the larger number of interfaces would act to enhance this effect.

### III. NANOCOMPOSITE $\text{SmCo}_5\text{:Nb}_{0.33}\text{Cr}_{0.67}$

Nanocomposites can be made with either non-magnetic or magnetic matrix materials, depending on the properties desired of the final material. By varying the magnetic character of the component materials, a wide range of final magnetic properties may be achieved.

Our chosen matrix material is  $\text{Nb}_{33}\text{Cr}_{67}$ . Mechanical alloying of  $\text{Nb}_{33}\text{Cr}_{67}$  for extended periods of time results in an amorphous structure which, upon annealing at a sufficiently high temperature, crystallizes as  $\text{NbCr}_2$ . This crystallization temperature is expected to be higher than that of amorphous (or nanocrystalline)  $\text{SmCo}_5$ , making it an ideal matrix material for annealing experiments. The  $\text{SmCo}_5$  is 6.25 vol.% of the final composite, which should result in well-isolated particles with limited magnetic interaction. Measurements of nanocomposites with two pre-milling times (2 hours and 15 hours) are reported here. The 2-hour premill has the maximum coercivity (16 kOe) observed; however, at some temperatures, the samples are not saturated at the

maximum available field of 55 kOe and the prominence of the exchange anisotropy and/or exchange-spring effects may complicate interpretation of results. In contrast, the 15-hour premill (which has a coercivity of 3.4 kOe) was chosen due to the lack of a significant anisotropy shift and the presence of complete saturation of the magnetization. X-Ray diffraction measurements of the nanocomposites show only peaks from crystallites of Nb and Cr.

Fig. 4 shows the percent change in the coercivity from the value of the premilled  $\text{SmCo}_5$  as a function of alloying time.

$$\% \text{ change} = \frac{H_c(\text{premilled SmCo}_5) - H_c(\text{nanocomposite})}{H_c(\text{premilled SmCo}_5)}$$

Data from the 15-hour premilled samples are shown as squares, with solid symbols representing aligned measurements and open symbols representing unaligned measurements. Circular symbols represent the 2-hour premilled samples.

The coercivity in the 15-hour premilled samples increases briefly before decreasing, whereas the 2-hour premilled samples show no initial increase. The rate of decrease in  $H_c$  is less for both than for  $\text{SmCo}_5$  samples premilled for a comparable total time. Comparison of  $\text{SmCo}_5$  milled for 16 hours with the 15-hour pre-mill/1-hour alloy samples shows that the  $\text{SmCo}_5:\text{Nb}_{33}\text{Cr}_{67}$  nanocomposite has a slightly higher coercivity and remanence than the premilled  $\text{SmCo}_5$ . For both samples, the remanence behaves analogously to the coercivity. The remanence decreases, but at a slower rate than if the  $\text{SmCo}_5$  had continued to be premilled by itself. The slow rate of decrease of the 15-hour premilled samples indicates that the primary effect of mechanical alloying in these samples is dispersion of the  $\text{SmCo}_5$  particles in the matrix. The faster rate of decrease in

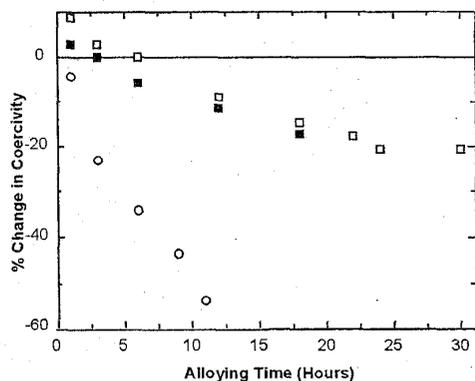


Fig. 4. Percent change in the coercivity of nanocomposited samples as defined in the text. 15-hour premilled samples are shown as squares and 2-hour premilled samples as circles. Aligned measurements are shown as solid symbols and unaligned measurements as open symbols.

the 2-hour premilled samples suggests that some refinement of  $\text{SmCo}_5$  particle size is still occurring. The values of the coercivity and the remanence ratio for both types of samples are not significantly affected by exposure to air prior to measurement. The saturation magnetization decreases to 90% of the value for samples not exposed to air.

#### IV. CONCLUSION

The coercivity of mechanically milled  $\text{SmCo}_5$  increases by a factor of five (to 16 kOe) during the first two hours of milling, followed by a slow decrease. The magnitudes of the coercivities indicate that significant regions of  $\text{SmCo}_5$  are present, despite the likelihood of small amounts of oxidation. An enhanced remanence ratio independent of particle alignment is also observed. These effects may be a result of exchange anisotropy due to ferromagnetic-antiferromagnetic interactions (most likely due to small amounts of CoO) and/or exchange-spring phenomena due to exchange coupling of hard and soft ferromagnetic regions ( $\text{SmCo}/\text{Co}$ ). The large number of surfaces present in mechanically alloyed materials would enhance both effects.

Nanocomposites formed by mechanically alloying premilled  $\text{SmCo}_5$  with a powder mixture of  $\text{Nb}_{33}\text{Cr}_{67}$  show that, when the ferromagnetic particles are small enough, the primary effect of alloying is to disperse the particles throughout the matrix material. Judicious selection of matrix material, premilling time and magnetic particle concentration can be used to tailor the magnetic properties of the final material to the desired specifications. The NbCr matrix material used here allows handling in air without significantly compromising the magnetic properties of the ultrafine rare earth powder. Proper selection of matrix materials provides an additional variable for tailoring by allowing controlled annealing.

#### REFERENCES

- [1] Yinong Liu, M.P. Dallimore, P.G. McCormick and T. Alonso, "High coercivity  $\text{SmCo}_5$  synthesized by chemical reduction during mechanical alloying", *J. Magn. Magn. Mat.* **116**, L320 (1992)
- [2] J. Ding, P.G. McCormick and R. Street, "Structure and magnetic properties of mechanically alloyed  $\text{Sm}_x\text{Co}_{1-x}$ ", *J. Alloys and Compounds* **191**, 197 (1993)
- [3] P. Ganesan, H. K. Kuo, A. Saavedra and R.J. DeAngelis, "Particle size distribution function of supported metal catalysts by x-ray diffraction" *J. Catalysis* **52**, 310 (1978)
- [4] J.S. Jacobs and C.P. Bean, "Fine particles, thin films and exchange anisotropy", in *Magnetism*, vol. III, G.T. Rado and H. Suhl, Eds. New York: Academic, 1963 pp 271-350 (and references therein)
- [5] Eckhart F. Kneller, "The exchange-spring magnet: A new material principle for permanent magnets", *IEEE Trans. Magn.* **27**, 3588 (1991)