Magnetic Properties of Mechanically-Alloyed Sm–Co Nanophase Hard Magnets

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Abstract—Highly coercive $\text{Sm}_{14}\text{Co}_{86}$ powders were prepared by mechanical alloying with a view to enhance the high temperature magnetic properties by optimizing the annealing conditions. The powders were annealed in quartz tubes with a continuous vacuum of $\sim 10^{-6}$ mbar at different temperatures. X-Ray diffraction studies confirmed the formation of a disordered 2:17 phase. DTA measurement on the as-milled amorphous powders revealed a single crystallization event at around 500 °C. Magnetic measurements showed room temperature coercivities of at least 1 T and Curie temperatures around 820 °C. The behavior of the initial magnetization curve lies in between those observed for low H_c 2:17 precipitation hardened magnets and SmCo_5 or $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets. The magnitude of coercivity is found to be sensitive to annealing temperature. The detailed comparison of magnetic properties with annealing conditions will be presented.

Index Terms—High temperature applications, mechanically alloyed materials, rare earth permanent magnets, Sm–Co based permanent magnets.

I. INTRODUCTION

IN BOTH the United States and Europe, the search for new high temperature permanent magnets has become a key issue which has led to resurgence in interest in $\text{Sm}_2\text{Co}_{17}$ type magnets. The normal approach to development of coercivity, H_c , in these precipitation-hardened bulk magnets is to develop nanophase cellular microstructures with cell walls that act as pinning sites [1]. In mechanically alloyed magnetic materials, additional crystallographic defects are introduced which lead to a higher coercivity [2], while remanence enhancement has also been observed [3]. Extensive studies were performed on Sm–Co nanocrystalline powders prepared by mechanical alloying [4], but they did not examine high temperature properties of the materials. The purpose of our current work is to enhance the high temperature properties of $\text{Sm}_{14}\text{Co}_{86}$, which in an intermediate composition between the SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ compositions, through optimization of annealing temperature.

II. EXPERIMENTAL

$\text{Sm}_{14}\text{Co}_{86}$ (nominal composition) samples were mechanically alloyed from a mixture of SmCo_5 and 99.8% pure Co powder. The SmCo_5 , obtained from Less Common Metals, Merseyside, England in ingot form, was broken up and crushed

under an argon atmosphere before milling. The milling was carried out under an argon atmosphere for 12 hours in a high energy Spex 8000 mixer/mill with a ball to powder charge ratio of 9.3 : 1.

As-milled powders were subjected to a subsequent annealing at various temperatures between 650 °C and 850 °C. The annealing treatment was carried out in quartz tubes which were continuously evacuated during annealing to maintain a vacuum on the order of 10^{-6} mbar. Two different methods for annealing were tested. In method I, the furnace was preheated to the desired temperature and then the sample was pushed into the hot zone of the furnace. After the desired length of time, the tube was removed from the hot furnace and allowed to cool in air (with the sample still under vacuum). In method II, the tube was pushed into the furnace at room temperature and then heated at 10 °C/min to the desired temperature. The tube was held at the chosen temperature for the desired length of time, and then cooled inside the furnace at a rate of 5 °C/min.

Chemical and oxygen/nitrogen analysis confirmed that the contamination of the samples was negligible, with <5 wt% Fe, <0.1 wt%, <0.06 wt% N_2 , and <0.25 wt% O_2 . The $\text{Sm}_{14}\text{Co}_{86}$ nominal composition samples were shown to actually contain 26.5 wt% Sm after milling and annealing, rather than 29.4 wt%, giving an actual composition closer to $\text{Sm}_{12.4}\text{Co}_{87.6}$.

Powder x-ray diffraction (XRD) was carried out on both as-milled and annealed powders using a Siemens D500 XRD with $\text{Cu-K}\alpha$ radiation. Crystallization behavior of the as-milled powders was studied using a Stanton–Redcroft DTA with a heating rate of 10 °C/min under Ar flowing at 25 cm^3/min . Scanning Electron Microscopy (SEM) was used to study powder morphology. Samples for room temperature magnetic hysteresis measurements were prepared by mixing approximately 20 mg of annealed powder with Lecoset 7007 cold curing resin inside a 4 mm by 4 mm cylindrical Perspex bucket. After the epoxy had cured, samples were magnetized in an 8 T pulsed field before measuring hysteresis loops in a vibrating sample magnetometer up to 1.0 T applied field. Measurement of hysteresis loops in fields greater than 1.1 T was carried out using an extraction magnetometer.

III. RESULTS AND DISCUSSION

Typical powder x-ray diffraction patterns for the as-milled materials showed only a broad hump around $44^\circ 2\theta$, as shown in Fig. 1. This is indicative of an amorphous structure. SEM showed the powder particles to be roughly spherical, with a rough surface. Individual particles range from a few micrometers in size up to 20 μm , while agglomerations of particles could

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Fig. 1. Typical Cu-K α X-Ray diffraction patterns for as-milled Sm₁₄Co₈₆ samples and samples annealed at 700 °C and 800 °C. As-milled samples exhibit an amorphous structure which crystallizes to a disordered Sm₂Co₁₇ structure at annealing temperatures ≥ 500 °C. At annealing temperatures ≥ 800 °C, there is Sm loss which is evidenced by the appearance of fcc Co peaks in the XRD patterns.

be up to 50 μm in size. This morphology is consistent with previous observations for mechanically alloyed materials [5], [6].

The DTA trace on heating the as-milled Sm₁₄Co₈₆ displayed a peak at around 440 °C, where the amorphous phase undergoes crystallization. X-Ray diffraction of samples annealed just above this temperature showed this peak to be indicative of crystallization of Sm₂Co₁₇ from the amorphous material.

The X-Ray diffraction pattern for the sample annealed at 700 °C, shown in Fig. 1, is typical of those for samples annealed at $650\text{ °C} \leq T_{\text{ann}} < 800\text{ °C}$. The pattern is characteristic of Sm₂Co₁₇, in that it contains only the main reflections which are shared by both rhombohedral (Th₂Zn₁₇) type and hexagonal (Th₂Ni₁₇) type phases. The samples probably consist of a single phase with random sections of rhombohedral and hexagonal stacking sequences. For samples annealed at $T_{\text{ann}} \geq 800$ °C, there is a loss of Sm due to vaporization. This is evidenced by a metallic coating on the quartz tube after annealing and the appearance of small peaks around 45° and $52^\circ 2\theta$ in the X-Ray diffraction pattern (Fig. 1). These peaks are characteristic of fcc Co. Hysteresis loops for the samples annealed at $T_{\text{ann}} \geq 800$ °C indicate that the fcc Co phase is exchange coupled to the Sm₂Co₁₇ phase. The Curie temperature (T_c) of the samples, determined by magnetic measurements, is around 820 °C.

Hysteresis loops comparing the two annealing methods are shown in Fig. 2. Both samples were annealed at 750 °C, in method I for 30 min, but for only 15 min in method II. The sample annealed with method II shows a much larger coercivity than the sample annealed with method I.

After choosing method II as the better annealing method, a study of the effect of annealing temperature on the magnetic properties of mechanically alloyed Sm₁₄Co₈₆ was carried out. Samples were annealed using method II at temperatures $650\text{ °C} \leq T_{\text{ann}} \leq 850$ °C for 15 minutes. H_c peaks for T_{ann} between

Fig. 2. Hysteresis loops comparing two different annealing routes for mechanically alloyed Sm₁₄Co₈₆. In both methods the samples were loaded into a quartz tube which was continuously evacuated during annealing to a pressure of 10^{-6} mbar. In method I, the furnace was preheated to 750 °C and then the sample was pushed into the hot furnace. After 30 min, the tube was removed from the hot furnace and allowed to cool in air (with the sample still under vacuum). In method II, the tube was pushed into the cool (room temperature) furnace and then heated at $10^\circ/\text{min}$ to 750 °C. The tube was held at temperature for the desired length of time, and then cooled inside the furnace at a rate of $5^\circ/\text{min}$.

Fig. 3. Magnetic properties of mechanically alloyed Sm₁₄Co₈₆ as a function of annealing temperature.

750 °C and 800 °C (Fig. 3). This behavior suggests that the optimum temperature range for annealing to develop a microstructure with high coercivity lies between 750 °C and 800 °C.

One sample was annealed twice using method II with $T_{\text{ann}} = 700$ °C for 30 min each time. Interestingly, this sample presents a high coercivity of 1.1 T, shown by the hysteresis loop in Fig. 4. The behavior of the initial magnetization curve lies in between those observed for low H_c 2:17 precipitation hardened magnets and SmCo₅ [8], suggesting a mixture of pinning-type and nucleation-type behavior. The enhanced M_r/M_s ratio (>0.5) indicates the existence of intergrain exchange interactions among the fine grains [7]. In addition, the hysteresis loop shows a smooth demagnetization curve, indicating a very fine and uniform grain size in the samples.

Fig. 4. Hysteresis loop for $H(T)$ mechanically alloyed $\text{Sm}_{14}\text{Co}_{86}$ annealed twice at 700°C for 30 min using annealing method II, which involves slow heating and cooling steps.

IV. CONCLUSIONS

Our current studies show that the coercivity of mechanically alloyed $\text{Sm}_{14}\text{Co}_{86}$ powders can be dramatically increased by optimizing the annealing temperature and the method of annealing. The as-milled powder particles were roughly spherical and chemical analysis showed negligible contamination from the milling container and balls and oxygen. The as-milled powders crystallized to a disordered $\text{Sm}_2\text{Co}_{17}$ structure at annealing temperatures less than 800°C . Above that temperature there was vaporization of Sm, as evidenced by the appearance of fcc Co peaks in the X-Ray diffraction pattern.

Two different annealing routes were tested and it was found that an annealing process starting with a slow heat and ending

with a slow cool was the better route to optimize the microstructure. A study using the slow heat/slow cool method and varying the annealing temperature showed that the best H_c is achieved with annealing temperatures between 750°C and 800°C .

A coercivity of 1.1 T was achieved for a mechanically alloyed $\text{Sm}_{14}\text{Co}_{86}$ sample which had been annealed twice at 700°C for 30 min with a slow heat and slow cool each time. This indicates that longer annealing times and/or a second annealing step may be necessary for coercivity development in these materials.

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