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Structure and magnetic properties of mechanically alloyed Sm_xCo_{1-x}

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Abstract

A study of the phase structure and magnetic properties of mechanically alloyed and heat-treated Sm_xCo_{1-x} with $x=0.13$ to 0.24 has been carried out. Remanence enhancement above 0.5 M_s (M_s = saturation magnetisation) was found in samples with $x=0.12$ to 0.17 after annealing at 700 °C. A maximum energy product of 16.6 M G Oe was measured for $Sm_{0.13}Co_{0.87}$. Coercive forces above 50 kOe were obtained for $x=0.17$–0.20 after heat treatment at approximately 800 °C. The highest value of 57 kOe was measured for $Sm_{0.19}Co_{0.81}$.

1. Introduction

Sm–Co magnets based on the $SmCo_5$ and Sm_2Co_{17} phases have been widely used since their discovery in the 1960s [1]. Both phases exhibit high Curie temperatures and high values of saturation magnetisation and anisotropy field.

The synthesis of a number of rare earth–transition metal alloys by mechanical alloying has been reported recently [2–8]. Optimally heat-treated structures have been shown to exhibit exceptionally high coercivities and isotropic behaviour associated with nanocrystalline microstructures. Wecker *et al.* [6] obtained coercive forces of 30 kOe and 6 kOe respectively in mechanically alloyed $SmCo_5$ and Sm_2Co_{17}. Liu *et al.* [7, 8] recently reported the direct synthesis of $SmCo_5$ by the chemical reduction of Sm_2Co_3 and SmF_3 during mechanical alloying. Giant coercive forces of over 65 kOe were exhibited in specimens prepared from SmF_3 [8]. In this paper we report the results of a study of the effect of Sm concentration and heat treatment on the structure and magnetic properties of mechanically alloyed Sm–Co alloys.

2. Experimental details

The starting materials used in this study were 99.9% pure Sm (−40 mesh) and Co (−50 mesh) powders. The mechanical alloying was performed in a hardened steel vial with three 12 mm steel balls for 12 h. The as-milled powders were pressed into disk-shaped specimens, which were heat treated for 30 min at temperatures of 500–1000 °C under a vacuum of 2×10^{-7} Torr [5].

The powders were examined by X-ray diffraction using a Siemens D5000 diffractometer with monochromatic CuKα radiation. Magnetic properties were measured at room temperature using a vibrating sample magnetometer (type VSM3001, Oxford Instrument Company) with a maximum applied field of 120 kOe.

3. Results and discussion

3.1. Structure

All powders after mechanical alloying were found to be amorphous on examination with X-ray diffraction, as indicated in Fig. 1 for the as-milled $Sm_{0.15}Co_{0.85}$ powder.

Crystallisation occurred on heating to 500–600 °C for all of the mechanically alloyed powders. The X-ray diffraction patterns indicated that powders consisted of randomly oriented nanocrystalline grains. The average powder particle size was estimated from scanning electron microscopy (SEM) to be approximately 1 μm.

For the Sm concentration $x=0.15$, which is lower than the Sm concentration of the stoichiometric composition of $SmCo_5$ (*i.e.* $Sm_{0.167}Co_{0.833}$), the $TbCu_7$-type phase [9] (disordered Sm_2Co_{17} phase) was formed as a main phase after heat treatment at annealing temperatures, T_a, less than 800 °C. This is shown in Fig. 1. At higher annealing temperatures, a mixture of $SmCo_5$ ($CaCu_5$ structure) and Sm_2Co_{17} (Th_2Zn_{17} structure) [1] was found (Fig. 1).

Saito *et al.* [10] have reported the formation of the $TbCu_7$-type phase in Sm_2Co_{17} ribbons prepared using melt-spinning at high roll velocities. The Th_2Zn_{17}-type

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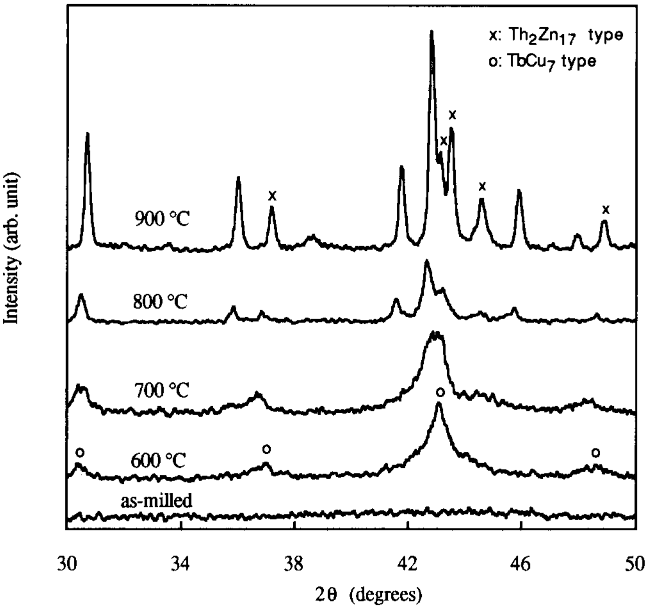

Fig. 1. X-ray diffraction patterns of $Sm_{0.15}Co_{0.85}$ powders as-milled and annealed at 600–900 °C for 30 min.

phase was the dominant phase at low roll velocities. The magnetic properties of the $TbCu_7$-type phase (*i.e.* Curie temperature, saturation magnetisation and anisotropy field) are similar to those of the Sm_2Co_{17} phase [10].

For Sm concentrations, $x = 0.17$–0.18, the X-ray diffraction patterns indicated that a mixture of the $TbCu_7$-type and the $CaCu_5$-type phases was formed at annealing temperatures below 800 °C. Heat treatment at $T_a \geq 800$ °C led to the formation of nearly single $SmCo_5$ phase in powders for compositions of Sm_xCo_{1-x} with $x = 0.17$–0.19. A very small amount of Sm_2Co_{17} with the Th_2Zn_{17} structure was also present in powders with $x = 0.17$ and 0.18.

Samples of Sm_xCo_{1-x} with $x = 0.2$–0.22 contained $SmCo_5$ and Sm_2Co_7 (Ce_2Ni_7 structure) [1] after annealing between 600 °C and 900 °C. As expected, the amount of the 2–7 phase in $Sm_{0.22}Co_{0.78}$ was significantly larger than in $Sm_{0.2}Co_{0.8}$. This 2–7 phase possesses a high anisotropic field (greater than 220 kOe [11]), similar to that for $SmCo_5$ (about 300 kOe [1]). The magnetic moment per Co atom has been estimated to be approximately equal to that for $SmCo_5$ [12]. The lower saturation magnetisation of 600–700 G for the 2–7 phase [13] relative to that for $SmCo_5$ (891 G at room temperature) is the result of the higher Sm content, since Sm has a much lower magnetic moment per atom (about 0.5 μ_B [12]) than that of Co atoms.

The $SmCo_3$ phase was identified as the main phase in $Sm_{0.24}Co_{0.76}$ powders at annealing temperatures of 600–900 °C. Minor phases of Sm_2Co_7 and $SmCo_5$ were also found in the powders. The amount of these minor phases increased with increasing annealing temperature, due to Sm vaporisation.

3.2. Magnetic properties

Samples of $Sm_{0.15}Co_{0.85}$ exhibited a relatively high magnetic remanence M_r of about 600 G after heat treatment at 600–700 °C. This value is higher than that expected of an aggregate of randomly oriented grains, for which M_r should equal 0.5 M_s. (The values of saturation magnetisation are 891 G and 995 G for the $SmCo_5$ and Sm_2Co_{17} phases respectively [1].) Remanence enhancement was also found in $Sm_{0.13}Co_{0.87}$ powders after annealing at 600–700 °C. In these samples M_r was measured to be greater than 700 G (Fig. 2), which is about 70% of the saturation magnetisation for Sm_2Co_{17} ($M_s = 995$ G). The maximum magnetisation of 961 G for this sample measured at 120 kOe is very close to M_s.

The remanence enhancement observed here is similar to that reported by Coehoorn *et al.* [15] who found that the remanence of $Nd_4Fe_{78}B_{18}$, which contained mainly the soft magnetic phase Fe_3B and about 15% hard magnetic $Nd_2Fe_{14}B$ phase after crystallising amorphous melt-spun ribbons at 675 °C, reached 955 G (1.2 T) corresponding to 70–80% of M_s. This sample also exhibited a coercivity of 3 kOe, which is not expected for a material containing 85% of the soft magnetic phase Fe_3B, if the demagnetisation of the soft phase is independent of the presence of 15% of the hard magnetic phase $Nd_2Fe_{14}B$. This enhancement of M_r above 50% of M_s for melt-spun Nd–Fe–B ribbons with low Nd concentration has also been observed by other authors [16–18] and has been explained by the exchange interaction associated with a nanoscale mixture of two

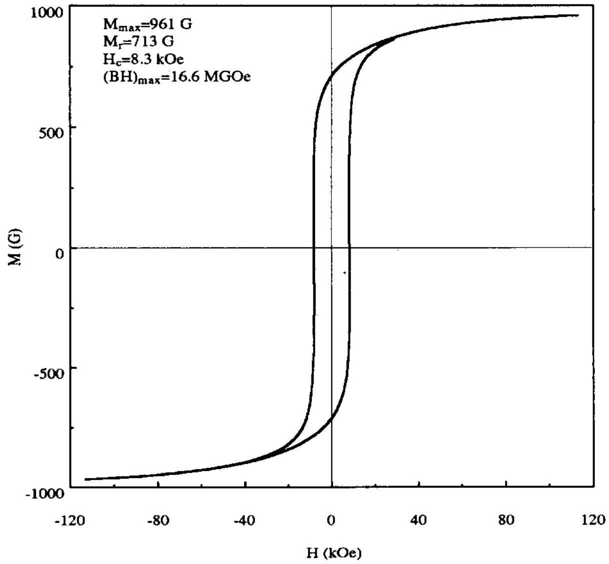

Fig. 2. Hysteresis loop of $Sm_{0.13}Co_{0.87}$ annealed for 30 min at 700 °C.

or three phases [15–18]. Manaf *et al.* [19] have found that the enhancement of M_r above $0.5 M_s$ can be obtained in melt-spun Nd–Fe–B ribbons consisting of nearly single $Nd_2Fe_{14}B$ phase, if the ribbons contained very small grains ($M_r = 1.13$ T for ribbons with grain size of less than 30 nm [19]). The enhancement of the remanence in the Sm_xCo_{1-x} system observed here can be similarly explained by the exchange interaction between nanocrystalline grains of the $TbCu_7$-type and $SmCo_5$ phases, while a very small grain size of about 5 nm (for Sm_xCo_{1-x} with $x = 0.13$ and $x = 0.15$ after a heat treatment at 600 °C) was estimated using transmission electron microscopy.

The enhancement of the remanence to above $0.5 M_s$ significantly increased the maximum energy product $(BH)_{max}$. The highest value was found to be 16.6 M G Oe for $Sm_{0.13}Co_{0.87}$. In comparison, the $(BH)_{max}$ of isotropic samples with $M_r = 0.5 M_s$ equals 10 M G Oe (*i.e.* 25% of the theoretical $(BH)_{max}$ value [1]). The shape of the hysteresis loop (Fig. 2) is very similar to those of Nd–Fe–B ribbons with high remanence resulting from grain interaction [15–19]. The $Sm_{0.15}Co_{0.85}$ samples annealed at 600–700 °C possessed a higher coercive force of 20–25 kOe. However, the $(BH)_{max}$ value of about 13 M G Oe was lower than that for $Sm_{0.13}Co_{0.87}$, because of the lower remanence for $Sm_{0.15}Co_{0.85}$. The values of $(BH)_{max}$ for $Sm_{0.15}Co_{0.85}$ powders decreased with increasing annealing temperature, apparently because of the effect of increasing grain size. The $(BH)_{max}$ value of 8.4 M G Oe after annealing at 900 °C is less than that for isotropic $SmCo_5$.

Remanence enhancement was also observed for the higher Sm concentrations of $x = 0.17$ and $x = 0.18$ (Fig. 3). Samples annealed at $T_a < 800$ °C contained a mixture of the $SmCo_5$ phase and the $TbCu_7$-type phase, and the hysteresis loops were similar to that shown in Fig. 2. The energy product values were about 13 M G Oe and 10 M G Oe for $x = 0.17$ and $x = 0.18$ respectively, while coercive forces of 25–35 kOe were observed. The enhancement of the remanence was not so large as that for lower Sm concentrations ($x = 0.11$–0.15), because of the increase of the amount of the $SmCo_5$ phase. The ratio of M_r/M_s decreased with the Sm concentration.

As shown in Fig. 3, the coercivity values increased sharply with increasing T_a from about 30 kOe at $T_a = 700$ °C to 50–55 kOe at $T_a \geq 800$ °C for $x = 0.17$ and $x = 0.18$ (Fig. 3). This increase in H_c is associated with the phase transition from a mixture of the $TbCu_7$-type phase and the $SmCo_5$ phase into nearly single $SmCo_5$ phase with a very small amount of the Th_2Zn_{17}-type phase. The hysteresis loops for samples annealed at $T_a \geq 800$ °C clearly showed two independent phases associated with the presence of Sm_2Co_{17} (causing a small step and having coercive force of 7–8 kOe) and $SmCo_5$. The remanence of 400–450 G was near that of isotropic samples without grain interaction (*i.e.* $0.5 M_s$). The slight increase of M_r with the annealing temperature in the range 800–1000 °C in Fig. 3 was caused by the increasing amount of the Sm_2Co_{17} resulting from Sm vaporisation.

For samples of Sm_xCo_{1-x} with $x = 0.2$–0.24, H_c and M_r were not strongly dependent on the annealing temperature. For samples with $x = 0.2$, the remanence decreased somewhat with increasing annealing temperature, from 600 G for samples annealed at 600 °C to 540 G for samples heated at 800 °C. For higher Sm contents M_r was nearly independent of T_a.

In Fig. 4 the maximum value of H_c obtained at each composition is plotted as a function of x. High coercive forces of $H_c \geq 50$ kOe were achieved for Sm concen-

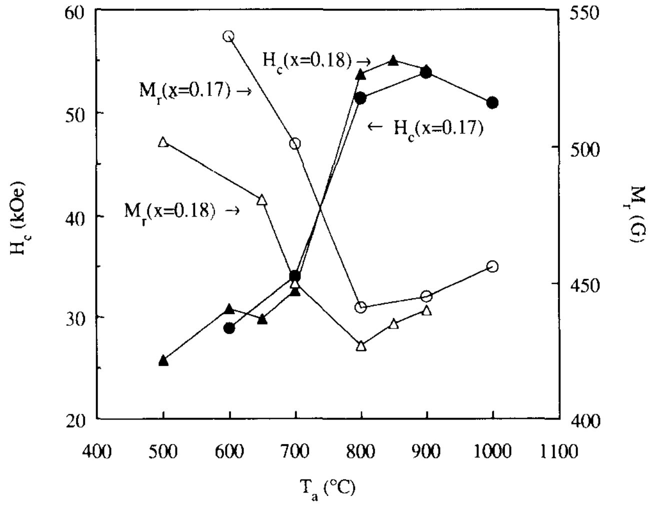

Fig. 3. Coercive force H_c and remanence M_r of Sm_xCo_{1-x} with $x = 0.17$ and $x = 0.18$ as a function of annealing for 30 min at temperatures T_a.

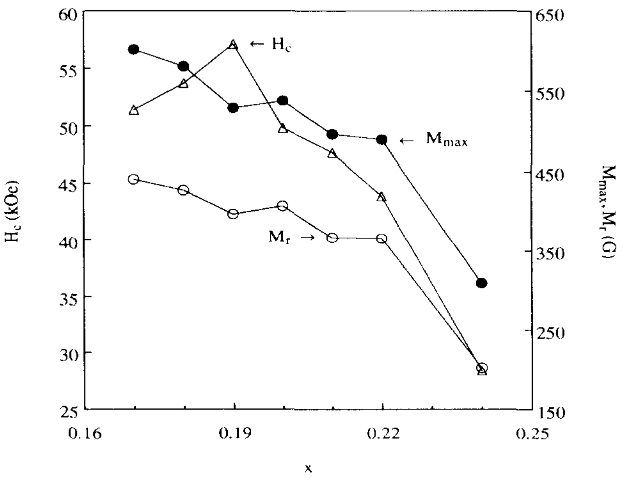

Fig. 4. The highest obtained coercive force H_c with the measured maximum magnetisation M_{max} (at 120 kOe) and the remanence M_r as a function of the Sm concentration x in Sm_xCo_{1-x} with $x = 0.17$–0.24.

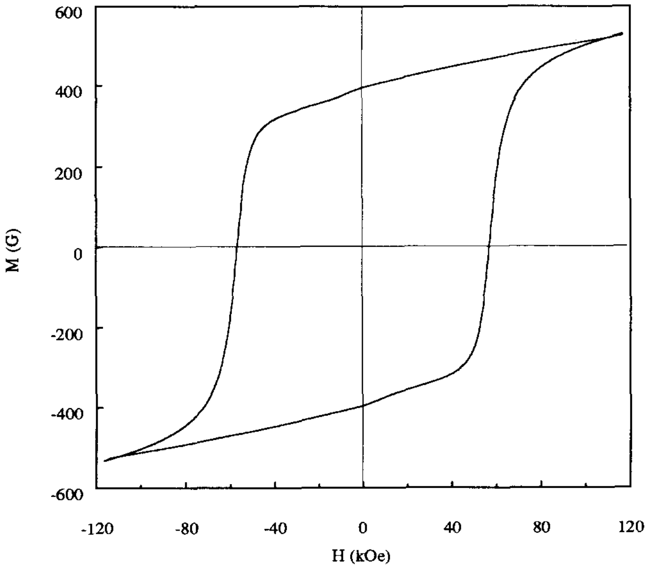

Fig. 5. Hysteresis loop of the $Sm_{0.19}Co_{0.81}$ sample after heat treatment for 30 min at 800 °C.

trations in the range $x=0.17$–0.20, in agreement with the findings of previous studies [1, 8, 20, 21], showing that a small excess of Sm over that required for stoichiometric $SmCo_5$ increases coercivity. The sharp decrease of H_c, M_r and the maximum magnetisation M_{max} (measured at 120 kOe) at $x=0.24$ results from the presence of $SmCo_3$, which has a low magnetic moment per Co atom and a low Curie temperature, as a main phase.

The highest coercive force H_c of 57.1 kOe was found for $Sm_{0.19}Co_{0.81}$ powder annealed at 800 °C (Fig. 5). The remanence of about 400 G was somewhat smaller than the theoretical value of about 450 G (0.5 M_s). Measurements of the remanence M_r and H_c as functions of the applied field showed that M_r and H_c were not saturated at the maximum applied field of 120 kOe, which is less than half of the anisotropy field for $SmCo_5$ (about 300 kOe [1]).

Similar giant coercive forces for $SmCo_5$ with a slight Sm excess have been reported previously, for example, $H_c=67.5$ kOe for plasma-sprayed film [20], $H_c=55$ kOe for sintered $SmCo_{5-y}$ samples [21] and 65 kOe for $SmCo_5$ synthesised by the reduction of SmF_3 [8] during mechanical alloying. Since the coercivity mechanism of sintered $SmCo_5$ magnets is generally accepted to be controlled by nucleation [1], it is of significance to study the coercivity mechanism for mechanically alloyed nanocrystalline $SmCo_5$ powders.

4. Summary

The magnetic behaviour of mechanically alloyed Sm_xCo_{1-x} alloys is dependent on the phases formed during crystallisation of the as-milled amorphous structure. For $x<0.19$ a mixture of the $TbCu_7$-type and $SmCo_5$ phases was formed after annealing at temperatures $T_a \leqslant 800$ °C; $SmCo_5$ and a small amount of the Sm_2Co_{17} phase were observed after heat treatment at $T_a \geqslant 800$ °C. Higher Sm concentrations with $x=0.2$–0.22 resulted in formation of the Sm_2Co_7 phase. For $x=0.24$, the $SmCo_3$ phase was found to be the main phase present.

Samples annealed at $T_a \leqslant 700$ °C exhibited remanence enhancements of about 0.7 M_s for $x=0.13$ and $x=0.15$, similar to that found in NdFeB alloys [15–19]. This behaviour appears to be the result of exchange interactions between magnetically coupled nanocrystalline phases. This remanence enhancement resulted in increased values of the maximum energy product $(BH)_{max}$, which was measured to be 16.6 M G Oe and 13.3 M G Oe for $Sm_{0.13}Co_{0.87}$ (annealed at 700 °C) and $Sm_{0.15}Co_{0.85}$ (annealed at 600 °C) respectively.

The sharp increase of the coercive force in samples of Sm_xCo_{1-x} with $x=0.17$–0.19, annealed at temperatures above 800 °C is associated with the formation of $SmCo_5$ nanocrystals as the principal phase. The highest coercive force H_c of 57.1 kOe was exhibited by $Sm_{0.19}Co_{0.81}$ samples annealed at 800 °C.

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