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Rare Earth Magnetic Materials Synthesized By Mechanical Alloying

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Since its discovery, mechanical alloying has demonstrated a significant potential for the processing of materials with novel structures and properties. Of particular interest has been the application of mechanical alloying to the synthesis of rare earth permanent magnet materials. In this paper the synthesis of $Nd_2Fe_{14}B$ and mixtures of $Sm_2Co_{17}/SmCo_5$ by the chemical reduction of rare earth oxides and fluorides is reported.

1. INTRODUCTION

Among the most promising applications of mechanical alloying is the synthesis of isotropic permanent magnet materials. Schultz and co-workers [1-4] first synthesized $Nd_2Fe_{14}B$, $SmCo_5$, $Sm_2Fe_{17}N_x$ and Sm-Fe-M (M=transition metal) alloy powders by mechanically milling pure metal powders of the constituent elements for each alloy. The magnetic phases were formed after a post-milling heat treatment. Ding et al. [5,6] studied the effects of composition and annealing/nitriding conditions on the magnetic properties of Sm-Fe-Nitride and Sm-Co powders synthesized by mechanical alloying. Alloys synthesized by mechanical alloying are generally found to exhibit isotropic magnetic properties which compare favourably with their commercial counterparts prepared by conventional methods. This is attributed to the very small crystal sizes resulting from high energy mechanical milling and low temperature heat treatment.

Recent studies have demonstrated that high energy mechanical milling is also capable of causing chemical reactions to allow the refining of pure metals directly from precursors such as oxides or halides [7,8]. In addition the rare earth permanent magnet alloys $SmCo_5$ and $Sm_2Fe_{17}N_x$ have been synthesized by mechanically milling Sm_2O_3 or SmF_3 with Ca and Co or Fe respectively [11-13]. This paper reports the direct synthesis of $Nd_2Fe_{14}B$ and mixtures of $Sm_2Co_{17}/SmCo_5$ from rare earth oxides and halides via chemical reactions by mechanical milling.

2. EXPERIMENTAL TECHNIQUES

The starting materials used in this study were Nd_2O_3, Sm_2O_3, SmF_3 and Fe powders all having a particle size of -325 mesh, Ca and Co (-50 mesh) and B. All materials were of 99.9% purity or better. Milling was carried out in a Spex 8000 mixer/mill for 24 hours using a hardened steel container with an O-ring type seal. The powders were sealed in the container in a high purity argon filled glovebox. Unloading of the milled powders and all further handling of the powder were carried out in the same environment. The milling

media consisted of ten hardened steel balls 12 mm in diameter, giving a 10/1 ball to powder mass ratio.

The as-milled powders were annealed at 1000-1150 K in a vacuum of $2x10^{-5}$ kPa for times up to 7.2 ks. The magnetic properties were measured on 5 mm diameter cold consolidated cylindrical samples. The measurements were carried out at room temperature using an Oxford Instruments Vibrating Sample Magnetometer (VSM3001) with a maximum applied field of 120 kOe. The structures of the as-milled and annealed powders were analysed by x-ray diffraction using a Philips PW1050 x-ray diffractometer and monochromatic CuKa radiation.

3. RESULTS AND DISCUSSION

3.1 $Nd_2Fe_{14}B$

$Nd_2Fe_{14}B$ was synthesized by mechanically milling a mixture of Nd_2O_3, Ca, Fe and B according to the reaction

$$Nd_2O_3 + 3Ca + 14Fe + B \rightarrow Nd_2Fe_{14}B + 3CaO \quad (1)$$

for 24 hours. The actual atomic ratio of Nd/Fe used was 2/10.5. A 30% excess of Ca and 100% of B were also employed. X-ray diffraction showed that the as-milled powder consisted of a-Fe and an amorphous phase (Fig. 1(a)). Annealing at 975 K for 1.8 ks resulted in the formation of $Nd_2Fe_{14}B$ from the as-milled two phase mixture as shown in Fig. 1(b). Diffraction peaks for the reaction by-product CaO were present in the patterns of both the as-milled and crystalised samples.

A magnetization hysteresis curve for the annealed sample is shown in Fig. 2. The curve indicates single phase magnetisation behaviour and the coercivity is 13.1 kOe. The saturation and remanent magnetizations were measured to be 93.6 and 61.8 emu/g respectively, at an applied field of 50 kOe.

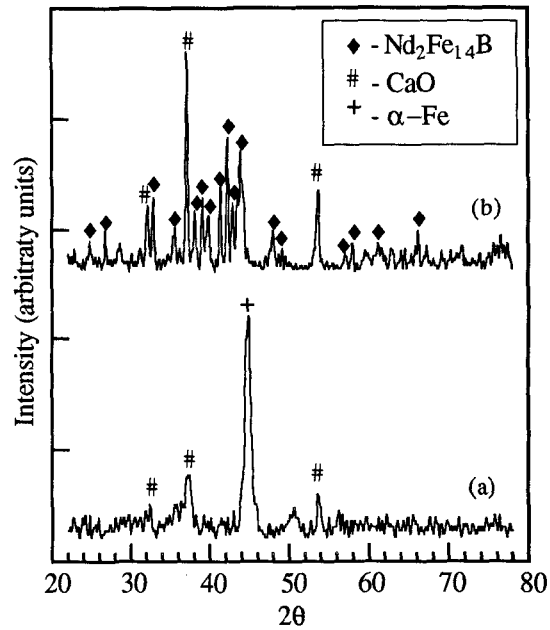

Figure 1. X-ray diffraction pattern of $Nd_2Fe_{14}B$ prepared via reaction (1) above: (a) as milled, (b) after annealing at 975 k for 1.8 ks.

These values correspond to saturation and remanent magnetizations of 1.26 T and 0.83 T, respectively, for the volume of the $Nd_2Fe_{14}B$ phase estimated from the reaction stoichiometry to be present in the sample. The maximum energy product for the volume of $Nd_2Fe_{14}B$ present is estimated to be 13.7 MGOe.

The structures following milling and crystallisation, and the magnetic properties of $Nd_2Fe_{14}B$ produced in this study by the chemical reduction of the Nd_2O_3 precursor agree well with that reported by Schultz et al. [1] in samples prepared by mechanical alloying the elements. In fact the annealing conditions adopted in this study correspond to that used in reference [1] to obtain maximum coercivity. The excess Nd/Fe ratio is also

similar to that used by this reference, and it is clear that an excess of Nd over stoichiometry is required to compensate for Nd losses resulting from oxidation and vaporisation occurring during processing.

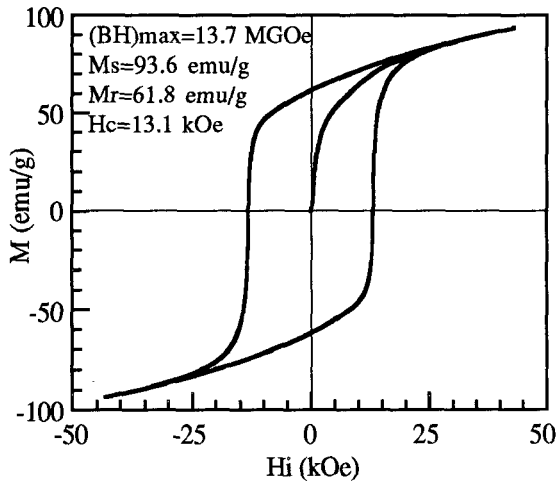

Figure 2. Magnetisation hysteresis curve of $Nd_2Fe_{14}B$ prepared via reaction (1) above.

3.2 $Sm_2Co_{17}/SmCo_5$

Sm-Co alloys were synthesized via two reduction reactions:

$$Sm_2O_3 + 3Ca + nCo \rightarrow Sm_2Co_{17} + (SmCo_5) + 3CaO \quad (2)$$

$$2SmF_3 + 3Ca + nCo \rightarrow Sm_2Co_{17} + (SmCo_5) + 3CaF_2 \quad (3)$$

For both reactions a 33% excess of Ca was used to ensure a complete reduction of Sm_2O_3. In the first reaction a Sm/Co atomic ratio of 2/13 was used to compensate for expected Sm losses during processing. In the second reaction the Sm/Co ratio was increased to 1/5. X-ray diffraction patterns of the as-milled samples showed only very broad humps centred at the major diffraction peaks for Sm_2Co_{17}, $SmCo_5$ and CaO or CaF_2. After annealing the as-milled powder at 1003 K for 2.7 ks, the x-ray diffraction patterns show that crystallisation has occurred (Fig. 3.). For reaction (2), the main phase present after annealing was Sm_2Co_{17}. However, minor peaks corresponding to $SmCo_5$ were also present, indicative of small net excess of Sm. For reaction (3) the diffraction pattern shows that an increased fraction of $SmCo_5$ present.

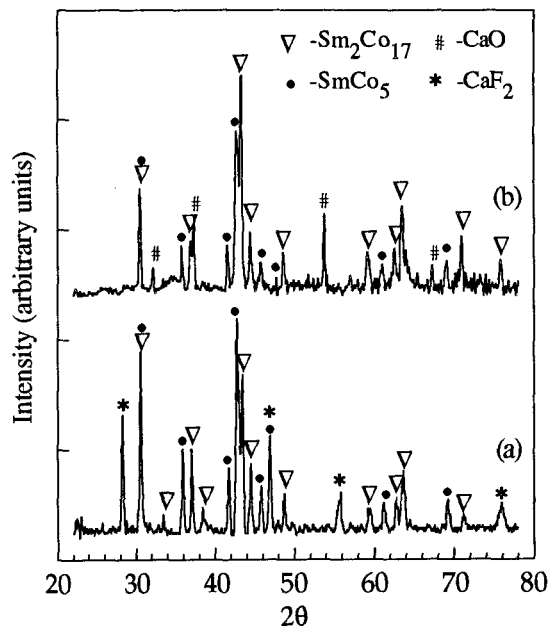

Figure 3. X-ray diffraction patterns of the $Sm_2Co_{17}/SmCo_5$ alloys produced via, (a) reaction (2) and (b) reaction (3) above.

The magnetization curves for samples from the two reactions, samples (a) and (b), are shown in Fig.4. The curves reflect the varying stoichiometry used in the two reactions. Sample (a) exhibited remanence and coercivity values of 56 emu/g and 16 kOe respectively, and for (b) the corresponding values were 55 emu/g and 28 kOe. The higher coercivity and lower remanence of (b) relative to (a) is consistent with the higher fraction of $SmCo_5$ present due to the higher Sm/Co ratio.

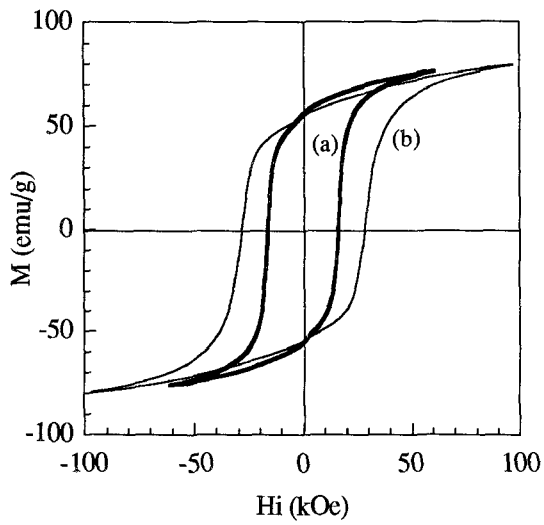

Figure 4. Magnetisation hysteresis curves of the $Sm_2Co_{17}/SmCo_5$ alloys produced via, (a) reaction (2) and (b) reaction (3) above.

Although the x-ray diffraction measurements show that both samples consist of two phase $Sm_2Co_{17}/SmCo_5$ structures the magnetization curves clearly indicate single phase magnetic behaviour. Similar results have been reported for $Sm_2Co_{17}/SmCo_5$ mixtures synthesized by mechanical alloying of Sm and Co metal. Such behaviour has been rationalised as due to exchange coupling across interphase boundaries of the nanocrystalline grains formed after heat treatment. Ding et al. found that mechanically alloyed mixtures of Sm_2Co_{17} and $SmCo_5$ exhibited single phase magnetic behaviour when crystalised at temperatures below 1023 K and two phase behaviour when crystalised at higher temperatures. The occurrence of two phase magnetic behaviour was associated with grain growth. In this study single phase magnetic behaviour has been observed in samples reduced using SmF_3 annealed at 1133 K. The preservation of single phase behaviour in samples annealed at the higher annealing temperature is presumably due to the inhibiting effect of CaF_2 crystallites on grain growth.

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