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Structural and Mössbauer studies on mechanical milled $SmCo_5$/α-Fe nanocomposite magnetic powders

P. Saravanan, M. Manivel Raja, R. Gopalan*, N.V. Rama Rao, K. Suresh, D.V. Sridhara Rao, V. Chandrasekaran

Defence Metallurgical Research Laboratory, Kanchanbagh P.O., Hyderabad 500 058, India

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Abstract

The $SmCo_5$/α-Fe nanocomposite powders were prepared by high energy ball milling and the inter-diffusion reaction between the $SmCo_5$ and α-Fe magnetic phases were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM) and ^{57}Fe Mössbauer spectroscopy. While structural and magnetic measurements could reveal only the presence of $SmCo_5$ and α-Fe phases, Mössbauer studies could clearly specify the extent of alloying between Fe and Co atoms in terms of evolution of α-Fe(Co) phase as a function of milling time. It has been found that the fractional volume of α-Fe(Co) solid solution tends to increase at the expense of the initial α-Fe phase upon progressive milling.

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1. Introduction

Efforts are underway to improve the energy product $[(BH)_{max.}]$ and Curie temperature (T_c) of rare-earth permanent magnets through nanocomposite approach. The concept which lies behind the evolution of these novel magnetic materials arises from the possibility of spring exchange coupling between the hard and soft magnetic phases when their size is reduced to nanoscale. The combination of large saturation magnetization of the soft phase and the large coercivity of hard phase is predicted to produce nanocomposite with superior magnetic properties. Among the rare-earth permanent magnets, $SmCo_5$ has large magneto-crystalline anisotropy field (>240 kA/m) and also high T_c (∼1000 K). However, there are process limitations in realizing the energy product values of $SmCo_5$ magnets $[(BH)_{max.\ (theoretical)} = 1/4(\mu_0 M_s)^2 = 265\ kJ/m^3$, where μ_0 is permeability in free space and M_s is saturation magnetization]. In order to overcome this barrier, two-phase nanocomposite magnet comprising of $SmCo_5$ (hard) and FeCo (soft) magnetic phases seems to be more promising [1–3]. Recently, it has been demonstrated that enhanced magnetization can be obtained in mechanically milled and spark plasma sintered $SmCo_5 + 10–15$ wt% Fe nanocomposite magnet [4–6]. Despite the fact that Fe has very limited solubility in $SmCo_5$ phase [7], nearly a single-phase magnetic behavior is seen for the $SmCo_5$/α-Fe nanocomposite magnets—implying a strong magnetic coupling between the soft and hard phases [6,8]. It is presumed that during mechanical milling of $SmCo_5$ and Fe powders, some amount of Fe could be probably dissolved in the $SmCo_5$ crystal lattice. However, according to the Sm–Co–Fe phase equilibria, Fe has almost nil solubility in $SmCo_5$ phase [7] and hence it is important to understand the extent of the interaction that takes place between these two phases during milling. In general, structural/phase formation during mechanical alloying of $SmCo_5$ and Fe powders is studied mainly by X-ray

* Corresponding author. Tel./fax: +91 40 2434 0884.
E-mail address: rg_gopy@yahoo.com (R. Gopalan).

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diffraction and transmission electron microscopy. Each of these techniques has its own merits and demerits to exactly finger-print the formation of the Fe–Co phase, as the crystal structure of α-Fe and α-Fe(Co) are same. On the other hand, the Mössbauer spectroscopy is a powerful tool to investigate the local interactions between iron nuclei and their nearest neighbours through discrimination of the magnetic contributions of Fe, thus providing useful information regarding formation of the Fe(Co) phase. Recently, Blázquez et al. [9] have investigated the microstructure and local arrangements of Fe atoms that continuously evolve during ball milling of nanocrystalline Fe–Nb–(B,Ge) alloys using Mössbauer effect measurements. In the present work, we have investigated the effect of Fe addition on local structural changes that evolve during mechanical milling of $SmCo_5$ and α-Fe powders using Mössbauer spectroscopy and the results are discussed in complement with X-ray diffraction (XRD), transmission electron microscopy (TEM) and magnetization studies. Such a study is considered to be scientifically and technologically important for the development of $SmCo_5$/Fe nanocomposite magnets – as the occurrence of various magnetic phases such as α-Fe, $SmCo_5$ and $Sm(Co,Fe)_5$ during milling can significantly influence the magnetic properties of bulk magnets.

2. Experiment

The precursor $SmCo_5$ alloy was prepared by melting of elemental Sm and Co in high purity argon atmosphere. The alloy ingot was crushed into powder size of ∼300 μm and was mixed with commercially available α-Fe powders (Alfa Aesar; purity: 99.5%) having particle size less than 10 μm. The α-Fe powder of about 10 wt% was selected for mixing with $SmCo_5$ powder for ball milling, as this fraction of Fe has been reported to yield relatively high coercivity and magnetization in isotropic nanocomposite magnets [4,5]. Milling was performed in a planetary ball mill (FRITSCH pulverisette) with the milling vial and balls made of tungsten carbide. During ball milling, blocks of $Nd_2Fe_{14}B$ permanent magnets were fixed around the vial, to create a radial magnetic field inside the vial to synthesize anisotropic powders during milling. The milling time was varied typically from 2 to 30 h at a constant speed of 200 rpm with ball to powder ratio of 10:1. The progress of phase formation at various milling time was studied by X-ray diffraction (XRD) using a Philips diffractometer using Cu Kα radiation. High resolution transmission electron microscopy (model: FEI-TECNAI 20 UT) was used for microstructural studies of as-milled powders. Specimens for TEM studies were prepared by dimpling and ion milling in Gatan make Dual Ion Mill (model 600) at 5 kV. TEM specimens of powder samples were prepared by mixing in a high-temperature conducting polymer epoxy subsequently dried at 130 °C and a 3 mm disk was finally cut for ion milling. Magnetic properties of the powder samples were evaluated using a vibrating sample magnetometer (VSM) (ADE make, model EV9) up to a maximum field of 2 T. Mössbauer spectra were recorded using FAST comtec (German make) spectrometer at room temperature in a transmission geometry with a 25 mCi ^{57}Co source in Rhodium matrix. Prior to the experiments, the spectrometer was calibrated using a standard α-Fe foil of thickness 25 μm. The Mössbauer spectra of each milled powder sample were recorded for duration of about 5 days with total background counts up to $8-10 \times 10^5$. The Mössbauer spectra were fitted with the PCMOS-II least-square fit program [10].

3. Results and discussion

The XRD patterns of $SmCo_5$/α-Fe powder mixtures milled for different milling times are shown in Fig. 1. The milled powders essentially consist of two phases, *viz*. $SmCo_5$ (main phase) and α-Fe (minor phase) and there is no evidence for the presence of any oxide impurities. Upon increasing the milling time, broadening of XRD peaks and reduction in their intensities are observed owing to the grain refinement and strain accumulation induced during the milling process. The XRD peaks of the $SmCo_5$ and the Fe phases have overlapped after 10 h milling due to the broadening effect. Further, it is

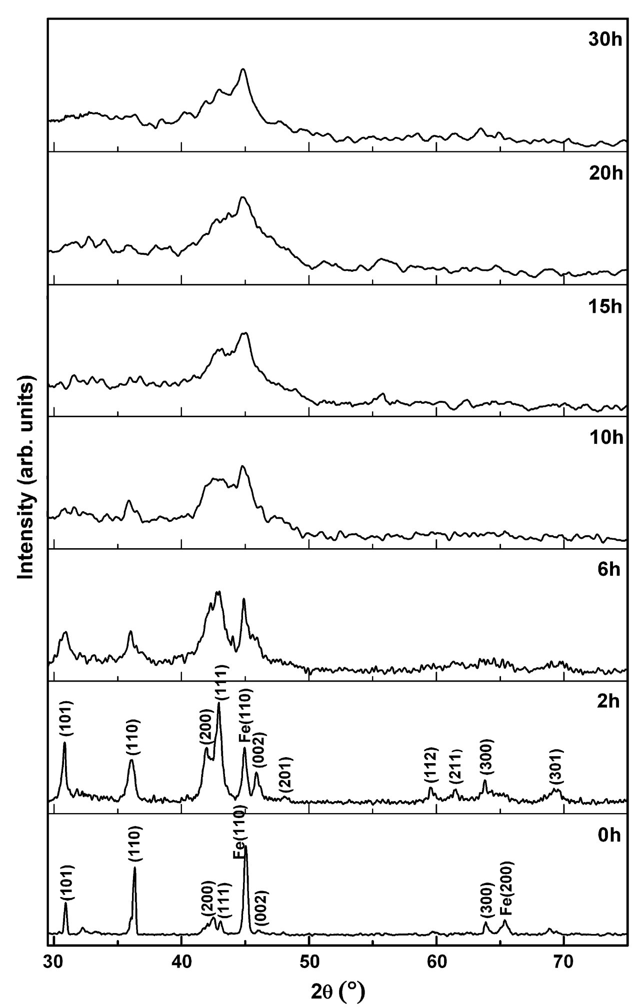

Fig. 1. X-ray diffraction patterns of as-milled $SmCo_5$/α-Fe nanocomposite powders for various milling times. The Miller indices of the main diffraction peaks are indicated in the figure.