Journal of Alloys and Compounds 509 (2011) 1065–1068

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Structure and magnetic properties of strontium ferrite anisotropic powder with nanocrystalline structure

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ARTICLE INFO

Article history:
Received 18 May 2010
Received in revised form
16 September 2010
Accepted 29 September 2010
Available online 8 October 2010

Keywords:
Strontium hexaferrite
Hard magnetic material
Nanocrystalline structure

ABSTRACT

The phase composition, nanocrystallite size, lattice microstrain and particles morphology of a $SrFe_{12}O_{19}$ powder subjected to milling and subsequent annealing were studied by various methods. The investigations showed that the high-temperature annealing of the preliminarily milled powder resulted in the increase in the coercive force ($\mu_0 H_{ci}$) of the $SrFe_{12}O_{19}$ powder up to 0.4 T owing to the formation of nanocrystalline structure ($D \sim 10^3$ nm) with low lattice microstrains. However, the annealed powder cannot be textured in an applied magnetic field because of random orientations of the crystallites in powder particles. A processing technique, which includes the low-temperature annealing of powder in an applied magnetic field, was suggested. It allowed us to produce the anisotropic powder of the strontium ferrite with the nanocrystalline structure that ensures the high coercive force of the powder (~0.4 T) and possibility of the powder texturing in the magnetic field. The prepared samples textured in a magnetic field exhibit the higher both remanence (by a factor of 1.4) and energy product (by a factor of 2.1) as compared to those of isotropic $SrFe_{12}O_{19}$ samples.

1. Introduction

Strontium hexaferrite magnets are widely used in electrotechnical and radio industry, computer and medicine technique owing to a favorable combination of sufficiently high magnetic properties, chemical stability and low cost [1,2]. It is well known that the coercive force of the hexaferrites depends mainly on the crystallite size; the high coercivity can be reached when the size of crystallites is $D \sim 100$ nm [3–6]. In our earlier work [6], we prepared $SrFe_{12}O_{19}$ powders having a sufficiently high coercive force $\mu_0 H_{ci} = 0.4$–0.45 T, which was explained by the formation of nanocrystalline structure. But the remanence of the powder was relatively low ($\mu_0 I_r = 0.25$ T) because of the random orientation of the nanocrystallites in the powder particles. The goal of our present work was to increase the remanence via preparation of the anisotropic powder, which is capable of texturing in the course of pressing in an applied magnetic field.

2. Experimental

As opposed to works [3–5], the coarse single-phase $SrFe_{12}O_{19}$ powder with a particle size $d \sim 10^1$ μm was used as the starting material. The milling was carried out in toluene medium in a SAND-1 planetary ball mill at a rotation speed of about 230 rpm using sealed vessels filled with hardened steel balls. The ball sizes were 2–10 mm, the ball-to-powder weight ratio was 10:1. The milling time was short ($t = 0.5$–2 h.). It should be noted that the milling time used in above mentioned works [3–5] was tens of hours.

The two-stage annealing of the milled powder included the low-temperature annealing in a temperature range of 270–460 °C which is below the Curie temperature of the $SrFe_{12}O_{19}$ phase ($T_C = 474$ °C) for 3 h and high-temperature annealing at a temperature of ~1000 °C for 1 h. The annealing was carried out in air in an external magnetic field (the magnetic field strength was $\mu_0 H > 0.9$ T) and in the absence of magnetic field using a laboratory furnace.

X-ray diffraction analysis of samples was performed using a computer-controlled diffractometer DRON-4 and CoKα radiation. Samples were prepared by pressing the powder in an applied magnetic field. The phase composition, polar density (0 0 1) function $2\pi p(\alpha)$, average crystallite sizes ($\langle D \rangle$) and lattice microstrain ($\langle e \rangle$) were determined by a reduced Rietveld method [7].

In addition, the size of powder particles and crystallites contained in these particles were studied by scanning electron microscopy (SEM) using a JEOL JSM-6700F electron microscope. The magnetic properties were measured at room temperature in external fields up to 2 T using a LDJ VSM–9600 vibrating sample magnetometer.

3. Results and discussion

According to X-ray diffraction data, the milling of the powder in the SAND-1 mill did not result in any changes in the phase composition: that is why, we called this treatment the low-energy ball milling in contrast to the high-energy ball milling [6], which changes the phase composition of the powder. As a result of the low-energy ball milling, the average crystallite size $\langle D \rangle$ of the $SrFe_{12}O_{19}$ phase, determined from the broadening of X-ray reflections, sharply decreases (to ~70 nm after 1 h milling); the lattice microstrain $\langle e \rangle$ increases (up to 0.3%).

The milling process also decreased the average size of powder particles. The average particle size of the initial powder was of an

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doi:10.1016/j.jallcom.2010.09.184

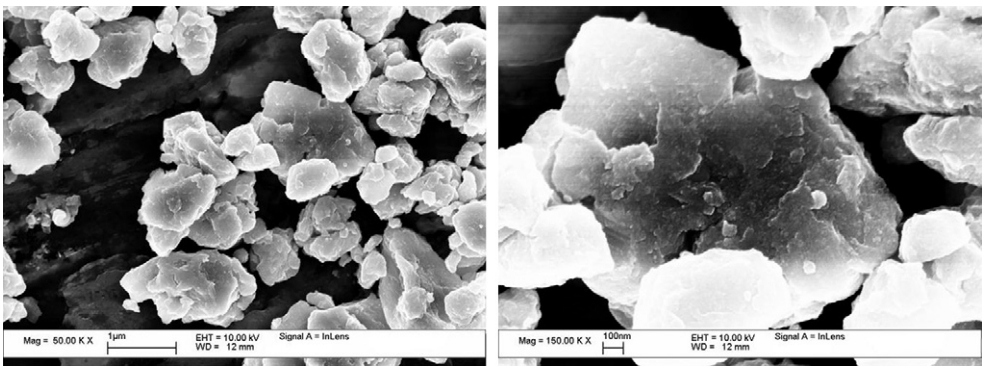

Fig. 1. SEM micrographs of the milled powder.

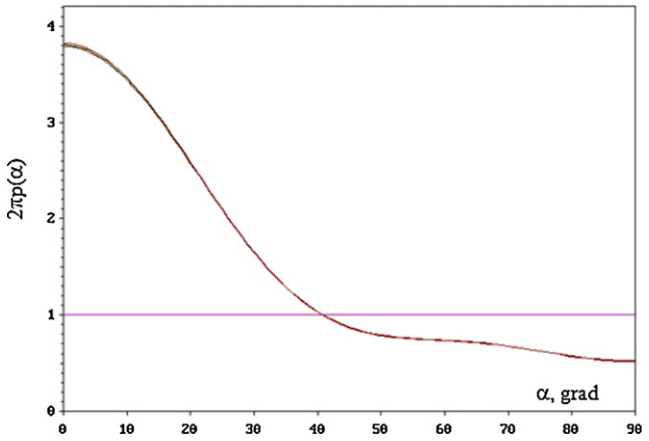

Fig. 2. Polar density (0 0 1) of the samples pressed in a magnetic field (PMF samples).

order of 10^1 μm, but after 1 h milling, it became $\sim 10^{-1}$–10^0 μm (Fig. 1)

The initial powder (before the milling) could not be textured by pressing in an applied magnetic field because of random orientation of crystallites in powder particles. It should be noted that the initial powder had the following magnetic properties: the intrinsic coercive force is $\mu_0 H_{ci} = 0.15$ T, the remanence is $\mu_0 I_r = 0.23$–0.25 T and the maximum energy product is $(BH)_{max} = 8.3$ kJ/m^3. The milling of the coarse powder in the SAND-1 mill provides the production of the powder consisting of single-crystal particles, which can be textured in an applied magnetic field. The texture formation (as a result of pressing the powder in an applied magnetic field) was proved by X-ray diffraction data (Fig. 2) and measurements of the magnetic properties of the samples (Fig. 3). These samples were obtained from the powder milled for 1 h.

The polar density (0 0 1) function $2\pi p(\alpha)$ (α is the angle between the ⟨0 0 1⟩ axis direction and normal to the sample surface) indicates the formation of ⟨0 0 1⟩ type axial texture in the samples (Fig. 2). For $\alpha = 0^O$, the value of $2\pi p(\alpha)$ function for the sample prepared by magnetic-filed pressing the powder milled for 1 h was significantly higher than unity; the remanence of this sample exceeds that of the isotropic sample by a factor of 1.6 (Fig. 3), i.e. the easy magnetization axis ⟨0 0 1⟩ of the milled strontium hexaferrite powder can be oriented along the magnetic field direction. The ability to form the texture in a magnetic field can be explained by the single-crystal structure of disperse particles of the milled powder. The milling of the powder, owing to the absence of changes in the phase structure, did not lead to significant variations of the intrinsic coercive force.

On the other hand, for any α, the value of $2\pi p(\alpha)$ function the for the sample prepared by pressing of the initial powder in a magnetic field was approximately equal to 1. This fact is the evidence of the absence of the texture in the sample. It was also confirmed by an analysis of the demagnetization curve of this sample. As is seen (Fig. 3a), the remanence of the strontium hexaferrite is approximately the half its saturation magnetization ($\mu_0 I_s \approx 0.48$ T) that corresponds to the isotropic structure of the sample.

To enhance the intrinsic coercive force and at the same time to hold the ability to form the texture in a magnetic field, the milled powder was subjected to two-stage annealing. This annealing included the low-temperature heat treatment curried out in an external magnetic field and high-temperature annealing in zero magnetic field. For comparison, the two-stage annealing was carried out also in the absence of magnetic field at the low-temperature stage.

The two-stage annealing (in an applied and zero magnetic field) led to the formation of strontium hexaferrite with the nanocrystalline structure with an average size of crystallites of ~100 nm (Fig. 4). It should be noted that, in the case of the hexaferrites, the critical size of single-domain particle is $D_c \leq 0.5$ μm [8]. Moreover, the annealing resulted in a sharp decrease in the $SrFe_{12}O_{19}$ lattice microstrain (up to 0.1%).

The annealing allowed us to increase the coercivity of the powder to values typical of the nanostructured state ($\mu_0 H_{ci} \approx 0.4$ T) [6].

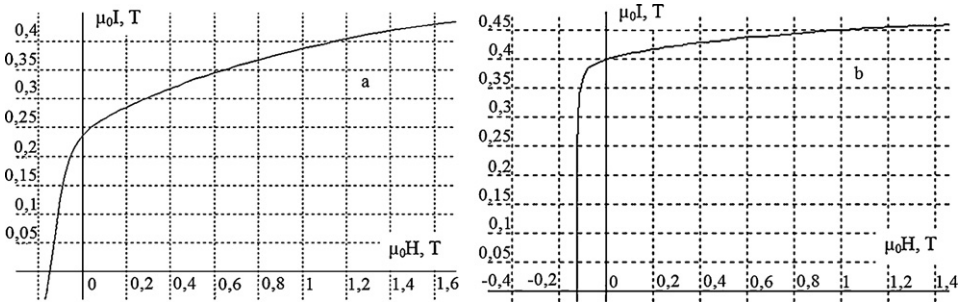

Fig. 3. Demagnetization curves of the PMF samples made from the (a) initial and (b) milled powders.

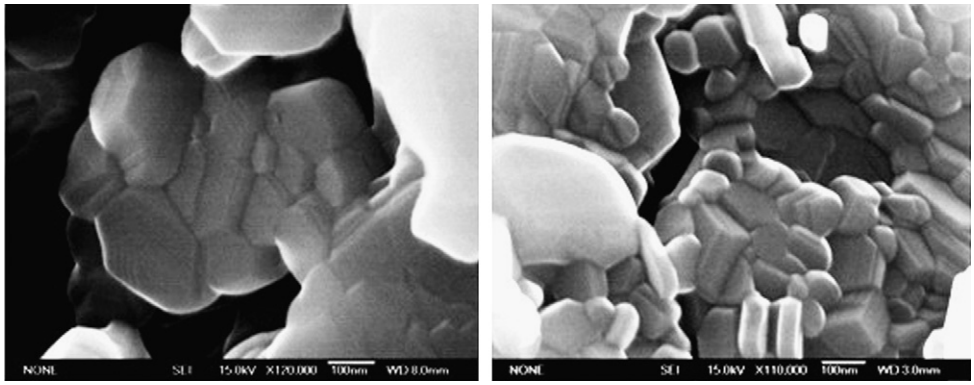

Fig. 4. SEM micrographs of the powder after two-stage annealing.

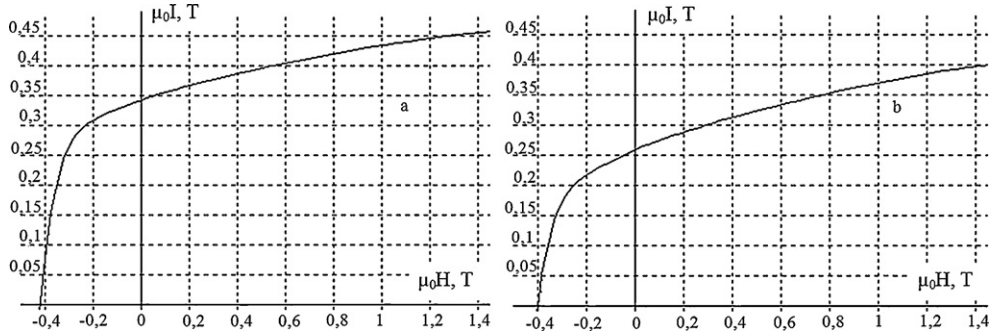

Fig. 5. Demagnetization curves of PMF samples made from the milled powder subjected to two-stage annealing in (a) an external magnetic field and (b) zero magnetic field.

As is seen from Fig. 5, along with the increase in the coercive force up to $\mu_0 H_{ci} \approx 0.4$ T, the remanent magnetization the PMF samples prepared from the powder annealed in a magnetic field significantly increases (by a factor 1.4) as compared to that of an isotropic (non-textured) sample. It should be noted that the remanence of initial powder was $\mu_0 I_r \approx 0.25$ T. Thus, the two-stage heat treatment including the low-temperature annealing in a magnetic field allowed the remanence to be considerably increased (up to 0.34 T).

The two-stage annealing allowed us to hold the ability of the strontium hexaferrite powder to be textured, i.e., its easy magnetization axis ⟨0 0 1⟩ to be oriented along the magnetic field direction. This was confirmed by not only the measurements of the magnetic properties but also X-ray diffraction texture analysis. Thus, we can conclude the anisotropic orientation of crystallites formed in the powder upon recrystallization in the course of the high-temperature annealing. The ability of the powder to form the texture in an external magnetic field disappears when the low-temperature annealing is carried out in zero magnetic field. Also it was shown that, if the annealing temperature an the low-temperature stage approaches the Curie temperature of the $SrFe_{12}O_{19}$ phase (T_C), the remanence decreases (Fig. 6), i.e. the perfection of the formed texture is reduced. Thus, the fact indicates the important role of magnetic interaction of the powder with an external magnetic field in processes of crystallite nucleation and growth upon annealing. At the same time, one can see from Fig. 6 that the coercive force of the powder is almost unchanged when the annealing temperature at the low-temperature stage approaches the Curie temperature of the $SrFe_{12}O_{19}$ phase. This means that, in contrast to the crystallites orientation, the size of crystallites is almost independent on the temperature (T_1, T_2, T_3) of the low-temperature annealing.

One can note that the maximum energy product of the powder after two-stage annealing in a magnetic field, was $(BH)_{max} = 18.4$ kJ/m^3 (Fig. 6).

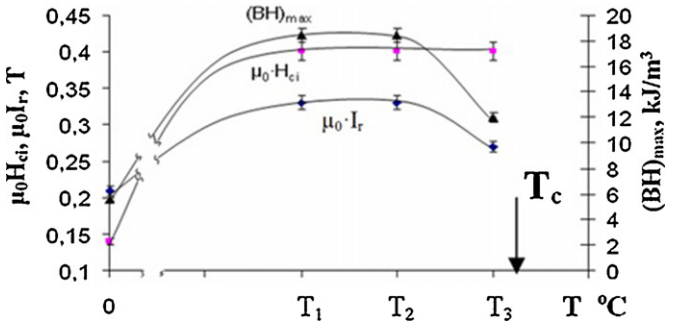

Fig. 6. Hard magnetic properties PMF samples as a function of the temperature at the low-temperature stage of two-stage annealing.

4. Conclusions

The two-stage annealing of the preliminarily milled coarse strontium hexaferrite powder and the use of a magnetic field at the low-temperature stage allow us to form the nanocrystalline structure that ensures the high intrinsic coercive force (about 0.4 T). At the same time the annealed powder can be textured in a magnetic field that permits us to increase the remanence (by a factor 1.4) and the energy product (by a factor 2.2) as compared to those of the isotropic nanocrystalline structure. This fact may be explained by the anisotropic orientation of $SrFe_{12}O_{19}$ nanocrystallites formed in the powder particles as a result of the annealing. This effect is not observed when the low-temperature annealing is carried out in zero magnetic field.

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