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Uniaxial anisotropy and enhanced magnetostriction of $CoFe_2O_4$ induced by reaction under uniaxial pressure with SPS

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ABSTRACT

In this study, we have compared magnetic and magnetostrictive properties of polycrystalline $CoFe_2O_4$ pellets, produced by three different methods, focusing on the use of Spark Plasma Sintering (SPS). This technique allows a very short heat treatment stage while a uniaxial pressure is applied. SPS was utilized to sinter cobalt ferrite but also to make the reaction and the sintering (reactive sintering) of the same ceramic composition. Magnetic and magnetostrictive measurements show that the reactive sintering with SPS induces a uniaxial anisotropy, while it is not the case with a simple sintering process. The induced anisotropy is then expected to be a consequence of the reaction under uniaxial pressure. This anisotropy enhanced the magnetostrictive properties of the sample, where a maximum longitudinal magnetostriction of −229 ppm is obtained. This process can be a promising alternative to the magnetic-annealing because of the short processing time required (22 min).

1. Introduction

In the recent years, there has been an increasing interest in improving magnetostriction of oxide-based materials, which are suitable alternative for rare earth alloys (such as Terfenol-D) due to their low cost, ease of fabrication and high electrical resistivity. Polycrystalline cobalt ferrite is an excellent candidate because various techniques of preparation permits an enhancement of the maximum longitudinal magnetostriction and piezomagnetic coefficient ($d\lambda/dH$). Both properties are essential to obtain actuators and sensors exhibiting great performances, which are the main applications for these materials. To achieve high magnetostrictive properties, the most common technique is to induce a magnetic anisotropy by applying a strong magnetic field during an annealing between 300 and 400 °C [1–5]. This permits a rearrangements of Co and Fe ions [6,7] and leads to a uniaxial anisotropy parallel to the direction of the magnetic annealing field, hence tuning the magnetostrictive properties. Wang et al. [8] proposed another technique in which particles were oriented through a magnetic field before the sintering, thus introducing a texture in the polycrystalline sample, which also contributes to better magnetostrictive properties. In this work, a new technique that induces uniaxial anisotropy is reported, based on a reaction under uniaxial pressure using Spark Plasma Sintering (SPS) method of production. SPS process allows the fabrication of high-density bodies at much lower temperature with short processing time. During the procedure, a high uniaxial pressure is applied while a pulsed electric current heats up the die and the sample [9]. SPS can be used either to activate the reaction [10] or to sinter [11,12] oxide-based materials. This paper will focus on the effect of reaction and/or sintering of the cobalt ferrite by SPS. Magnetic and magnetostrictive behavior of the distinct samples are then compared regarding the process of fabrication employed.

2. Experimental details

2.1. Samples fabrication

Polycrystalline $CoFe_2O_4$ samples were prepared by three different methods. In all the cases, nanosize (<50 nm) oxides Fe_2O_3 and Co_3O_4 (Sigma–Aldrich) were used as precursors in molar ratio of 3:1. Powders were mixed in a planetary ball mill during 30 min at 400 rpm, and then grinded during 1 h at 600 rpm. Initially, the classic ceramic method was used to produce our sample. Mixture was first calcined at 900 °C during 12 h to form the spinel phase, and then grinded at 550 rpm during 1 h. After uniaxial compaction at 50 MPa in a cylindrical die of 10 mm diameter, sample was sintered at 1250 °C during 10 h. This sample will be referred as CF-CM. In the second method, the synthesis of the spinel phase was achieved under the same condition as for the ceramic method. However, the sintering process was done by SPS. In all SPS experiments, a graphite

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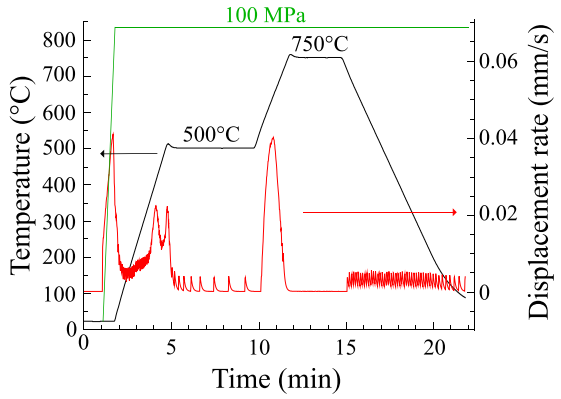

Fig. 1. Temperature (black), pressure (green) and displacement rate (red) profiles for the SPS process of the CF-RS-SPS sample. Stage at 500 °C correspond to the reaction and stage at 750 °C to the sintering. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

die of 10 mm diameter was used and the heating was carried out under neutral atmosphere (argon). The sintering was performed under a pressure of 100 MPa, with a 5 min temperature ramp from 20 °C to 980 °C followed by a stage of 2 min at 980 °C before cooling down. This sample will be referred as CF-S-SPS. Finally, in the last method, the SPS was utilized to make both the synthesis and the sintering (reactive sintering). The reaction stage was performed at 500 °C for 5 min and the sintering stage at 750 °C for 3 min, both under a pressure of 100 MPa. The thermal cycle was chosen based on the observation of the displacement rate of the pistons versus the temperature, as shown in Fig. 1. We assume that when the displacement rate brings back down, this signify that the reaction or sintering stage is well advanced, meaning that the temperature is properly chosen. This sample will be referred as CF-RS-SPS. Regardless of the method used, cylindrical pellets of 10 mm diameter and 2 mm thick were obtained.

2.2. Measurement procedures

The crystal structures of the ceramics were characterized by X-ray diffraction (XRD). XRD patterns of the samples were purchased from the pellets' surfaces and the experimental instrument employed is a Bruker D2 phaser 2nd Gen diffractometer using CoKα radiation. Diffraction patterns were recorded in the angular range from 15 ° to 100 ° with a scan step size of 0.02 °. The refinement is done by applying the Rietveld Method using MAUD software. The surface morphology are analysed using scanning electron microscope (SEM) Hitachi S-3400N model. A hydrostatic balance was utilized to determine the density of our ceramics. The magnetic measurements were carried out on samples, cut into cube shape of 8 mm^3, using a vibrating sample magnetometer (VSM, Lakeshore 7400) up to a maximum field of 1 T. Magnetostriction measurements were performed at room temperature by the strain gauge method with an electromagnet supplying a maximum field of 700 kA/m. The gauges were bonded on the pellets' surface along the direction (1) and the magnetic field was applied in the three directions (1), (2) and (3) of the Cartesian coordinate system, (1) and (2) being in the plane of the disc and (3) out of plane.

3. Results and discussion

3.1. Microstructure

All samples were initially characterized by X-Ray Diffraction analysis, and in all cases the desired cobalt ferrite spinel structure has been obtained, as shown in Fig. 2. To make sure that no

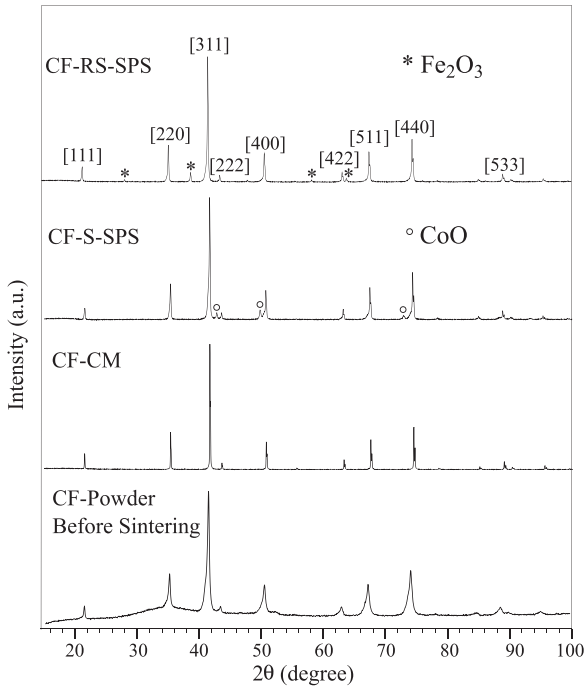

Fig. 2. XRD patterns of $CoFe_2O_4$ samples CF-RS-SPS, CF-S-SPS and CF-CM. The XRD results of the cobalt ferrite powder after calcination is also plotted.

Table 1
Results of structural and magnetic measurements of CF-CM, CF-S-SPS and CF-RS-SPS. Properties reported are: purity of the phase $CoFe_2O_4$, crystallite size ($<L_{XRD}>$), grain size ($<D_{SEM}>$), relative density (RD) of the sample, coercive field (H_c), remanent magnetization along the hard axis (M_r^{HA}) and the easy axis (M_r^{EA}), and saturation magnetization (M_s).

	Purity (wt%)	$<L_{XRD}>$ (nm)	$<D_{SEM}>$ (μm)	RD (%)	H_c (kA/m)	M_r^{HA} (mT)	M_r^{EA} (mT)	M_s (mT)
CF-CM	100	250 ± 25	4.2 ± 0.4	90	21	102	102	510
CF-S-SPS	93	120 ± 12	0.3 ± 0.1	97	19	229	229	505
CF-RS-SPS	91	100 ± 10		97	53	205	301	452

secondary phase was present after the calcination and before the sintering process of CF-CM and CF-S-SPS, the XRD analysis was also performed on the cobalt ferrite powder (Fig. 2) and pure spinel phase was obtained. However, on the ceramics, the only sample free from secondary phase is CF-CM. Purity of the spinel phase for each sample are reported Table 1. CF-S-SPS sample sintered at 980 °C presents a small amount of CoO phase (7 wt%). This secondary phase, already reported in previous papers [11,12], might be a result of partial reduction of the ferrite to CoO in the graphite die during the SPS sintering. CF-RS-SPS sample, obtained by reactive sintering, shows 9 wt% of hematite (Fe_2O_3). This can be a consequence of the precursor oxides Fe_2O_3 that did not completely react with the Co_3O_4 during the short reaction stage (5 min). From MAUD refinement, it was possible to retrieve the average crystallite size (precisely the size of coherent diffraction domain $<L_{XRD}>$) for each sample (see in Table 1). As expected, the size decreases with the reaction time and sintering time of the sample. To investigate the microstructure of the produced materials in more details, SEM observations were performed. The recorded SEM micrographs for the three different samples CF-CM, CF-S-SPS and CF-RS-SPS are shown in Fig. 3. It is apparent that CF-CM's grain size are much larger than for the sample CF-S-SPS, which was sintered with SPS. On the other hand, the grain size of CF-RS-SPS is not easily visible since SPS permits a short reaction time (5 min) thus little grain growth [10], the grain size might be of the order of 50 nm, as the precursor oxides, which is too small to be seen with our SEM model.

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