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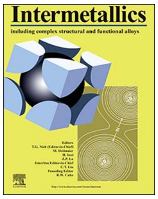

Magnetic property enhancement of cobalt-free M-type strontium hexagonal ferrites by $CaCO_3$ and SiO_2 addition

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ABSTRACT

An experiment was performed to investigate whether $CaCO_3$ and SiO_2 addition enhances the magnetic properties of cobalt-free M-type Sr ferrites, in which experimental parameters such as additive composition and the $CaCO_3/SiO_2$ ratio were changed. The specimens were prepared using conventional ceramic techniques. $CaCO_3$ addition promoted densification and uniform grain growth, resulting in high remanence; however, with the simultaneous addition of $CaCO_3$ and SiO_2, coercivity decreased to 3046 Oe in Sr ferrite hard magnets without Co_3O_4. SiO_2 addition suppressed grain growth. The addition of appropriate concentrations of $CaCO_3$ and SiO_2 as additives after calcination was shown to be very beneficial for tailoring a dense microstructure with relatively small grains. A $CaCO_3/SiO_2$ ratio of approximately 1.8 was found to be optimum, and the magnetic properties of B_r = 4.3 kG, iH_c = 3.7 kOe, and $(BH)_{max}$ = 4.5 MGOe were obtained for Sr ferrite hard magnets without Co_3O_4, which are acceptable for motor applications under output power < 1 kW.

1. Introduction

Many studies have evaluated the magnetic properties and synthesis of M-type hexagonal ferrites, which have a general formula of $MFe_{12}O_{19}$ (M = Pb, Sr, or Ba) and a magnetoplumbite structure [1–4]. Their distinct magnetic properties, such as high Curie temperature, high magnetization per formula unit ($20\mu_B$ at 0 K), high permeability, high coercivity (i.e., iH_c: intrinsic coercivity), excellent chemical stability, corrosion resistivity, and low production cost [4–6], have led to the increasing use of M-type ferrites in industrial applications such as rotors in brushless DC electric motors (BDCMs) [7].

For the use of M-type ferrites in BDCM applications, the development of ferrite grades with large coercivity (iH_c), large remanence (B_r), and maximum energy product ($(BH)_{max}$) is critical. The magnetic properties of M-type ferrites are mainly influenced by the stoichiometry, cation distribution in the crystal lattice, grain size, porosity, and anisotropic grain growth [8,9]. A large B_r requires a high sintered density and growth anisotropy, whereas large H_c requires a small grain size. In practice, to maintain the typical high-magnetic properties of Sr ferrites without lanthanum, the coercivity iH_c = 3.1–3.2 kOe and the remanence B_r = 4.0–4.2 kG are required. However, the aforementioned magnetic properties may be difficult to achieve because (1) the composition of ferrite is not identical to that of the stoichiometry of $SrO{\cdot}n(Fe_2O_3)$ with a mole ratio $n = 6$ (Sr hard ferrites are usually prepared with an excess of SrO) and (2) some unavoidable residual porosity leads to a decreasing sintered density and a nonideal anisotropy factor (α; or orientation ratio (OR)) of the particle. Importantly, a large remanence $B_r = 4\pi M_s{\cdot}\alpha{\cdot}\rho$ requires a large saturation magnetization $4\pi M_s$, high density ρ, and high anisotropy factor α. A large saturation magnetization $4\pi M_s$ is essential to precisely tailor the applicable raw material Fe_2O_3 (i.e., purity and specific surface area (SSA)) [7], suitable additives, calcined condition, and sintered condition. To obtain a high α, a sufficiently strong applied magnetic field is needed to align single-crystal particles during the wet pressing of powders. Because of strong crystalline anisotropy, the applied magnetic field overcomes the resistance of alignment to align the easy direction of magnetization of each particle. To increase orientation, dispersants can be added and mixed uniformly with the powders before the fine milling process. However, the shape anisotropy of the particle and the existence of particles containing multigrains reduce the degree of alignment, which must be avoided [10]. To manufacture hard ferrite with a large B_r, it is crucial to precisely tailor the material stoichiometry and the ceramic

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process to control the complex interplay between particle grain growth and the sintered density. By contrast, a large H_c can be achieved by absolutely eliminating magnetic domain boundaries with a grain size smaller than the critical size for a single-domain particle of approximately 1 μm [11,12]. The coercivity iH_c can be calculated as $iH_c = bH_a - N(B_r + J_s)/\mu_0$, where b, H_a, N, B_r, and J_s are the grain size factor, the magnetocrystalline anisotropy field, the grain demagnetizatiom factor, remanence, and the saturation magnetization, respectively [13–15]. Factor b increases with decreasing grain size. A trade-off always exists between the two magnetic properties of B_r and H_c.

A large B_r is more difficult to achieve than is a large iH_c. A high sintered density with an oriented and uniform distribution of grains can be achieved by adding sintering additives. Fang et al. [16] reported that the proper addition of SiO_2 as a sintering aid promoted the magnetic properties of M-type ferrites. Töpfer et al. showed that the simultaneous addition of $CaCO_3$ and SiO_2 was beneficial for tailoring relatively small grains with a high sintered density [17]. However, the magnetic properties described in the aforementioned studies are not sufficient to manufacture high-remanence hard ferrite magnets with a B_r of more than 4.4 kG without deteriorating coercivity (iH_c should be maintained at > 3.3 kOe). Hence, it is necessary to further investigate whether simultaneous $CaCO_3$ and SiO_2 addition significantly promotes the magnetic properties of sintered magnetic ferrites.

The abnormal growth of grains with a severe duplex structure is usually observed in M-type ferrites without additives and is more prominent at a sintering temperature higher than 1200 °C [17]. The grain boundary is a crucial factor determining the microstructure of sintered hard ferrites. SiO_2 can be applied as an additive to form a liquid phase for suppressing grain growth and enhancing the coercivity of hard ferrite [18,19]; however, a decreased sintered density results in decreased remanence. Thus, the simultaneous addition of $CaCO_3$ and SiO_2 is appropriate for moderating grain growth inhibition and promoting the sintered density. Moreover, $CaCO_3$ plays an important role in promoting grain anisotropy during the sintering process [20], which enhances remanence. Previous studies have revealed that the incorporation of $CaCO_3$ and SiO_2 additives to form a liquid phase at the grain boundary leads to the apparent suppression of abnormal grain growth and the uniform distribution of grains with lower porosity [20,21]. In this study, we achieved magnetic property optimization through $CaCO_3$ and SiO_2 addition without lanthanum addition. We also addressed the following major issues: (1) For magnetic property optimization, we determined the optimum additive concentrations of $CaCO_3$ and SiO_2 in Co_3O_4-containing Sr ferrite to prepare an anisotropic hard magnet with a remanence (B_r) of > 4.4 kG and a coercivity (iH_c) of > 3.3 kOe; (2) For reducing the manufacturing cost, we successfully determined the optimum additive concentrations of $CaCO_3$ and SiO_2 in Sr ferrite without Co_3O_4 to achieve a remanence (B_r) of > 4.3 kG and a coercivity (iH_c) of > 3.7 kOe.

2. Experimental procedures

2.1. Sample preparation

In this study, a nonstoichiometric Fe-deficient composition, $Sr\cdot 5.8(Fe_2O_3)$, was used. All Sr ferrite samples were prepared using the standard ceramic process. This study used the raw material of Fe_2O_3 with high purity and an SSA of 3.7 m^2/g that was manufactured using the acid recycle Ruthner process (China Steel Corporation, Taiwan). Another raw material, $SrCO_3$ (grade B, Solvay Barium Strontium GmbH, Germany), was wet mixed with Fe_2O_3 in an attritor; subsequently, the additives of 0.1 wt% SiO_2 and 0.1 wt% H_3BO_3 were incorporated simultaneously into the slurry and then granulated. A single phase of submicron-sized Sr ferrite powder was prepared by calcining a mixed batch at 1280 °C for 1 h. The calcined granules were coarse milled in a roller mill to obtain an average particle size of approximately 2.6 ± 0.1 μm to ensure the following fine mill process could be carried on effectively. Subsequently, various concentrations of Co_3O_4 (0.3 wt% for sample A; 0 wt% for samples B, C, D, and E), $CaCO_3$ (0.9 wt%), SiO_2 (0.4 wt%), and dispersant (0.5 wt%) were added, and the mixture was fine milled for 12 h in a stainless steel ball mill (batch size: 400 g ferrite powder, 9 kg steel ball [4.76 mm diameter], and 700 g water). This procedure guarantees a narrow particle size distribution with a mean particle size of approximately 0.6 μm, which is essential to achieve favorable magnetic properties. To study the influence of the additive concentration on the magnetic properties and microstructure of Sr ferrites, samples A, B, C, D, and E were prepared by adding 0.4 wt%, 0.4 wt%, 0.45 wt%, 0.5 wt%, and 0.55 wt% SiO_2, respectively. Moreover, 0.9 wt% $CaCO_3$ was simultaneously added to all samples. To increase the OR during the wet pressing of the powders, 0.5 wt% dispersant was added to enhance the particle alignment. The ferrite slurry was pressed in a magnetic field of 1.5 T (field parallel to the direction of pressure) into discs of Φ26.5 diameter and 13 mm height (based on Japanese Industrial Standard, JIS C2501). The pressed pellets were sintered at a peak temperature of 1235 °C for 1 h.

2.2. Measurements

X-ray diffraction (XRD, Cu-Kα radiation) was used for the phase identification of the calcined magnetic powder. The particle size of the calcined magnetic powder after coarse milling and fine milling was measured using a Sympatec laser scattering system with a dry dispersion unit (system Rodos). The magnetic properties (B_r, iH_c, and $(BH)_{max}$) of the sintered magnets were measured at room temperature by using an NIM-2000 HF Hysteresis graph meter (China National Measuring Science Research Institute) on polished discs. Scanning electron microscopy (SEM; Zeiss) was used to analyze the ceramic microstructures on the polished and thermally etched faces of the magnets (perpendicular to the applied pressure and field).

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 presents the XRD patterns for the sintered specimens of all Sr ferrite samples. Fig. 1 also shows the standard patterns for sintered hexagonal Sr ferrite. According to the Joint Committee Powder Diffraction Standards card 84-1531, the results clearly revealed that a hexaferrite phase was formed after calcining at 1280 °C and then sintering at 1235 °C, and they showed a single-phase hexagonal structure. From Fig. 1, all peaks can be ascribed to the M-type hexagonal structure (i.e., $SrO\cdot 5.8Fe_2O_3$) with the following Miller indices: (006), (008), (107), (114), (201), (203), (205), (206), (2010), (303), (2011), and (220). As indicated by Lotgering [22] and Kim [23], the growth anisotropy induced by chemical additives (i.e., $CaCO_3$) was quantitatively expressed by the relative intensity ratio (I_{008}/I_{107}) between the (008) and (107) diffraction peaks. Fig. 2 represents the relative intensity ratio calculated from the XRD patterns of Sr ferrite samples. A higher relative intensity ratio (I_{008}/I_{107}) implies larger growth anisotropy, thereby leading to a larger OR (or α) [23]. The relative intensity ratio (I_{008}/I_{107}) of randomly oriented ferrite powders was 0.22 [23]. Although the concentration of $CaCO_3$ was fixed at 0.9 wt%, samples A–E showed a high relative intensity ratio (I_{008}/I_{107}) of 0.340–0.368, suggesting that the addition of Ca after calcination promotes growth anisotropy during the sintering process. By contrast, it was found that the relative intensity ratio (I_{008}/I_{107}) decreased with increasing concentrations of SiO_2 but increased with the removal of Co_3O_4. This finding also implies that the influence of $CaCO_3$ on the relative intensity ratio (I_{008}/I_{107}) exhibits a downward trend with increasing SiO_2 or Co_3O_4 addition.

The effects of the composition of the calcined samples on the morphology of the grains were investigated, as illustrated in Fig. 3 and 4. According to the morphology shown in Fig. 3 (i.e., simultaneous SiO_2 and H_3BO_3 addition, and various molar ratios of Fe_2O_3/SrO from 5.6 to