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Influence of SiO_2 and CaO additions on the microstructure and magnetic properties of sintered Sr-hexaferrite

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Abstract

The effect of simultaneous addition of CaO and SiO_2 on the microstructure and magnetic properties of sintered SrO-excess Sr-hexaferrites was studied. Both additives markedly affect the grain growth behavior and the magnetic properties. CaO-additions promote densification, which results in increased remanence, but due to simultaneuous grain growth the coercivity drops to <100 kA/m. SiO_2 additions are known to suppress grain growth. Simultaneous addition of CaO and SiO_2 is shown to be very beneficial in tailoring a dense microstructure with relatively small grains. The ratio of CaO/SiO_2 was found to be optimum at about 1, and magnets with a remanence of 430 mT and a coercivity of 300 kA/m were obtained. Transmission electron microscopy (TEM) studies and investigations by energy-dispersive analysis of X-rays (EDX) in the scanning TEM (STEM) mode show that both CaO and SiO_2 are concentrated at grain boundaries and grain junctions forming an amorphous secondary phase.

Keywords: Ferrites; Hard magnets; Grain size; Grain boundaries; $S_5Fe_{12}O_{19}$

1. Introduction

Hard ferrites of the Ba- or Sr-hexaferrite system are the major permanent magnetic material. These magnets are manufactured on large scale worldwide (300.000 and 50.000 t per year in Europe in 1994[1]). Hard ferrites have been introduced as new technically important magnetic materials in the 1950.[2] Recently, Kools et al.[3] have reviewed the status of this mature family of ceramic materials. Nevertheless, the improvement of ferrite materials with respect to specific material parameters or application fields is still a vital field of research.

One crucial issue is the development of ferrite grades with large remanence and energy product. Standard hard ferrites are manufactured as anisotropic ferrites, i.e. the ferrite particles are oriented in a magnetic field during molding. A large remanence $B_R = J_S\alpha\rho$ requires a high density ρ and anisotropy factor α of the sintered microstructure. If both quantities approach 100% the remanence becomes equal to the saturation polarization J_S. With a saturation magnetization of 74.3 emu/g at room temperature for $SrFe_{12}O_{19}$[4] B_R of a sintered magnet is 0.476 T at maximum. In practice, the remanence of a typical high-remanence ferrite is B_R = 400–420 mT. This is due to (i) the composition being not that of a stochiometric ferrite $SrO{\cdot}6Fe_2O_3$ (magnets are prepared with an excess of SrO) and (ii) the particle orientation being non-ideal and some residual porosity remaining. For high-remanence materials it is essential to create a dense, anisotropic microstructure by firing at high temperature. On the other hand, grain growth is detrimental with respect to the coercivity because of the formation of multi-domain particles. A large coercivity requires small grains with a size

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smaller than the critical size for single domain particles of about 1 μm.[5] To produce magnets with large remanence and coercivity, it is essential to precisely tailor the ceramic process which in turn controls the complex interplay between a dense microstructure and grain growth. Ferrite powder particles should have dimensions below 1 μm to allow some unavoidable grain growth during sintering and to limit the grain size in the sintered magnets to a few microns. Taguchi[6] and Schwarzer et al.[7] reported on sub-micron powders prepared by improved calcination and milling procedures which allow the preparation of high-performance magnets with large remanence (B_R = 0.44 T). Substitution of La and Co for Sr and Fe has emerged as a different approach to increase the ferrite performance, high-remanence magnets with B_R = 0.45 T and H_{CI} > 300 kA/m have been introduced.[3,8]

The formation of the desired dense microstructure with small oriented grains is controlled by the addition of sintering additives. Several systems have been proposed by Arendt.[9] SiO_2 was introduced as grain growth inhibitor in hexaferrites.[10] The mechanism of the action of SiO_2 in ferrites was studied by Haberey and Kools.[11,12] The sintering behavior and mechanism of grain boundary motion hindrance was studied in detail by Kools[13,14] and a new mechanism of reaction induced grain growth impediment (RIGGI) has been proposed. Simultaneous addition of 0.45% CaO and 0–0.6% SiO_2 as another option to suppress grain growth has been investigated; a large remanence and a coercivity of 250 kA/m were obtained.[15] Moreover, there are some indications that the size of the additives might also play a crucial role in determining their effectiveness for microstructure control. Positive effects of fine-grained silica[16] and the uniform incorporation of Ca and Si utilizing a sol–gel route[17] were demonstrated.

In this paper we report on microstructural control of the magnetic properties by simultaneously adding CaO and SiO_2 in a concentration range from 0 to 1 wt.%. We address the following issues: (i) determination of the optimum additive concentrations and (ii) role of additives in microstructure formation. Using both additives we prepared anisotropic dense Sr-ferrite magnets with a remanence of B_R = 430–440 mT and a coercivity H_{CI} = 250–300 kA/m.

2. Experimental

2.1. Sample preparation

All ferrite samples were prepared using the standard ceramic process. The raw materials $SrCO_3$ (grade B, Solvay Barium Strontium GmbH, Hannover, Germany) and Fe_2O_3 (EKO Recycling GmbH, Eisenhüttenstadt, Germany) were mixed in a molar ratio $SrO:Fe_2O_3$ = 1:5.6–5.8 and granulated. The granules (3–10 mm diameter) were calcined at 1300 °C for 0.5 h. The calcined granules were coarse milled in a rotary vibration mill to a specific surface area of s = 1–2 m^2/g.

SiO_2 and $CaCO_3$ were added in various concentrations and then the ferrite powders were fine milled in an attrition mill for 24 h (batch size: 2 kg ferrite powder, 20 kg steel balls (3 mm diameter) and 3 l water). This procedure gives a powder with a mean particle size of about 1 μm and a specific surface of 11–12 m^2/g. To study the effect of the additive concentration on the ferrite microstructure samples SF0–SF2 were prepared without any, or with either 0.5 wt.% SiO_2 or CaO addition. In all other samples SiO_2 and CaO were added simultaneously, whereas the total additive concentration (SiO_2 + CaO) of samples SF3–SF7 is 1 wt.% (Table 1). The additives were characterized by their specific surface: SiO_2 (360 m^2/g) and $CaCO_3$ (8 m^2/g). The ferrite slurry was pressed in a magnetic field of 560 kA/m (field parallel to the direction of pressure) into discs of 52 mm in diameter and 4–6 mm in height. The samples were sintered at a peak temperature of 1200–1300 °C.

2.2. Measurements

The particle size of the powders was measured with a Sympatec laser scattering system with a dry dispersion unit (system Rodos). The specific surface of the powders was determined by adsorption of nitrogen in a BET apparatus (Micromeritics). The magnetic properties of the sintered magnets were measured at room temperature with a permagraph (Magnet-Meßtechnik Ballanyi) on polished discs. The ceramic microstructures were analyzed on polished and thermally etched faces of the magnets (parallel to the applied

Table 1
Concentration of additives, *S/C* ratio (SiO_2/CaO), magnetic properties and density of samples sintered at 1280 °C

Sample SF	SiO_2 (wt.%)	CaO (wt.%)	*S/C* ratio	Density (g/cm^3)	B_R (mT)	H_{IC} (kA/m)	BH_{max} (kJ/m^3)
0	–	–	–	5.03	430	156	–
1	0.50	–	–	4.79	387	296	–
2	–	0.50	–	5.02	433	116	–
3	0.75	0.25	3	4.96	421	284	32.8
4	0.60	0.40	1.5	4.93	415	300	31.6
5	0.50	0.50	1	4.98	424	282	32.6
6	0.40	0.60	0.67	5.05	436	178	26.8
7	0.25	0.75	0.33	4.79	413	118	15.2
8	0.60	0.60	1	4.97	406	289	29.2
9	0.80	0.60	1.33	4.93	398	320	28.7
10	1.00	0.60	1.67	4.94	406	301	28.8