Key Engineering Materials
ISSN: 1662-9795, Vol. 762, pp 257-262
doi:10.4028/www.scientific.net/KEM.762.257

Submitted: 2017-08-08
Accepted: 2017-10-02
Online: 2018-02-05

Characteristics of Sintered Materials Obtained from Ferrite Nanopowders Synthesised with Different Methods

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Keywords: $NiFe_2O_4$, $CoFe_2O_4$, nanoparticles, sintering, properties

Abstract. Ferrite materials, especially those containing nickel and cobalt, are popular due to their unique mechanical and magnetic properties. Single phase $NiFe_2O_4$ and $CoFe_2O_4$ nanopowders obtained by different methods were used for sintering studies. Chemical sol-gel self-propagating combustion method, co-precipitation technology combined with hydrothermal synthesis or spray-drying method, and high frequency plasma chemical synthesis have been used to synthesize ferrite nanopowders. Relatively dense (95-99%) materials with high saturation magnetization (M_S = 80-84 emu/g for $CoFe_2O_4$ and M_S = 46-48 emu/g for $NiFe_2O_4$) were obtained at 1100-1200 °C temperatures.

Introduction

Lately, ferrite materials have attracted a wide range of scientists due to their diverse applications. Ferrites are technologically important materials because of their unique electric, dielectric, electronic, mechanic, magnetic, optical, and catalytic properties. Ni and Co ferrites are characterized by good magnetic properties [1], low (for $NiFe_2O_4$) [2] or high (for $CoFe_2O_4$) [3] magnetic coercivity, high electrical resistivity, negligible eddy current loss for high-frequency electro-magnetic wave propagation [2], chemical stability, and fairly high mechanical hardness [4]. This makes them suitable for many technological applications, such as microwave devices, telecommunication applications, electric motors and generators, excellent core materials for power transformers in electronics, read/write heads for high speed digital tape [1], high-density information storage and recording devices etc. Ferrite materials find wide application as catalysts [5] and in photocatalysis [6]. Recently, ferrite materials are used to avoid and remove radio frequency disturbances in audio systems [4], as polarized ferroelectric ceramic in acoustic elements of underwater sound transducers [7], and as microwave absorbing materials [8], including ferrite containing radar absorbing colours for disguising military aircraft [9]. Recently, cobalt ferrite nanoparticles have also been known to be a photo-magnetic material, which shows interesting light-induced coercivity change [10].

It has been found that ferrites in nanocrystalline state often exhibit unique physical and mechanical properties when compared to coarse-grained polycrystalline materials [11]. It is well known that the microstructure, especially crystallite size, essentially determines the hysteresis loop of soft ferromagnetic materials [12]. It is known that properties of nanocrystalline ferrite materials, including dielectric constant, conductivity, permeability, and other magnetic properties, are sensitive to their microstructure [13] which, in turn, is sensitive to their production technique [14], i. e. the synthesis method [1]. Samples produced by different synthesis methods show different electrical and magnetic properties [4]. Therefore, many new techniques for production of nanoparticles are being developed.

In this work we have tried to summarize compaction results and material characteristics of ferrite nanopowders obtained by four methods: by chemical sol-gel self-propagating combustion method, by co-precipitation technology combined with hydrothermal synthesis or spray-drying method, and by high frequency plasma chemical synthesis.

Experimental

Two distinct ferrite types ($NiFe_2O_4$ and $CoFe_2O_4$) are obtained by four different methods. For this research nickel and cobalt ferrite nanopowders were prepared by chemical sol-gel self-propagating combustion (combust.) method [15], by co-precipitation technology combined with hydrothermal synthesis (hydrotherm.) [16] or spray-drying (spray) [17] method, and by high frequency plasma chemical synthesis (plasma) [18]. The ferrites were sintered, and their mechanical and magnetic properties were studied.

Ferrite nanopowders obtained by all methods where prepared for sintering as follows: 3 wt% stearic acid was mixed mechanically with ferrite nanopowder sample for 1 h in planetary mill (400 rpm, vessel material – ZrO_2, milling ball material – ZrO_2) using isopropanol as dispersing environment. Stearic acid was used for better pressing. After mixing samples were dried in an oven at 80 °C and sieved through a 200 µm sieve. For pressureless sintering samples where pressed (200 MPa) as tablets with 12 mm diameter, height – 4-6 mm. Stearic acid was burned out at 600 °C. Samples were sintered for 2 h at isothermal conditions in air atmosphere at temperature range 900-1300 °C (10 °C/min) in furnace *LHT-08/18* (*Nabertherm GmbH*).

All samples were analyzed using X-ray diffractometer *Advance 8* (*Bruker AXS*). Crystallite size was calculated using the Scherrer equation. Magnetic properties of the synthesized ferrites were analyzed by vibrating sample magnetometry (*VSM Lake Shore Cryotronics Inc.*, model *7404 VSM*). Specific surface area (SSA) was measured by BET single point method. The microstructure on fracture surfaces of the sintered material was investigated using scanning electron microscopes *Mira/Tescan* and *Tescan Lyra-3*. Density and open porosity of sintered samples was determined using Archimedes' method.

Results and Discussion

The characteristics of ferrite nanopowders used in this study are given in Table 1.

Table 1. Properties of ferrite nanopowders

Sample	SSA [m^2/g]	d_{50}* [nm]	Crystallite size [nm]	Phase composition	M_S [emu/g]	M_r [emu/g]	H_c [Oe]
$CoFe_2O_4$ (plasma)	29	39	40	$CoFe_2O_4$	75.4	32.0	780
$CoFe_2O_4$ (combust.)	37	31	20	$CoFe_2O_4$	53.4	20.3	1170
$CoFe_2O_4$ (hydrotherm.)	61	19	12	$CoFe_2O_4$	57.3	17.3	566
$CoFe_2O_4$ (spray)	84	-	-	p.a. $CoFe_2O_4$, FeO(OH)	-	-	-
$NiFe_2O_4$ (plasma)	29	38	40	$NiFe_2O_4$	44.2	10.0	74
$NiFe_2O_4$ (combust.)	43	26	10	$NiFe_2O_4$	29.0	6.0	140
$NiFe_2O_4$ (hydrotherm.)	42	26	22	$NiFe_2O_4$	39.0	2.6	23
$NiFe_2O_4$ (spray)	85	-	-	p.a. $NiFe_2O_4$, FeO(OH)	-	-	-

*average particle size calculated from SSA; p. a. – partially amorphous;
M_s – saturation magnetization; M_r – remanent magnetization; H_c – coercivity

It was found that all synthesized ferrites were nanocrystalline stoichiometric single phase powders with specific surface areas (SSA) in wide range 30-60 m^2/g that depended on the method of synthesis and calculated particle size of 20-40 nm. Crystallite size of ferrites was also in the range of 10-40 nm.

In the case of spray-drying high dispersity nanoparticles were obtained that consisted mainly of cobalt or nickel ferrite, iron hydroxide FeO(OH) and X-ray amorphous part [17]. The SSA for these samples was in a wide range – 80-90 m^2/g. Products obtained by spray-drying method obtained magnetic properties only after thermal treatment at 350-400 °C; at 550 °C the saturation magnetization of nickel ferrite is 16.9 emu/g, while for cobalt ferrite it is 51.3 emu/g. After spray-drying granules of sizes up to 10 µm and of calculated average particle size of 13-15 nm were obtained [17].

The finest particles were obtained by spray-drying, hydrothermal and sol-gel self-propagating combustion synthesis; whereas, powders obtained by the plasma synthesis had the widest distribution of particle size in the range of 20-100 nm with some particle reaching 200 nm.

Relative density of samples before sintering was 51-52% for plasma synthesized products and 31-33% for products obtained by other methods. This shows that ferrite nanopowders obtained by these methods are more difficult to compress because their particles are finer than those of plasma-synthesized ferrite powders.

Nanosized ferrite powders were sintered at 900-1300 °C. Ferrite density after heat treatment is shown in Table 2.

Table 2. Relative density and open porosity of ferrites depending on sintering temperature (after 2 h sintering)

Sample	Sintering temperature [°C]									
	900		1000		1100		1200		1300	
	ρ [%]	$P_{op.}$ [%]	ρ [%]	$P_{op.}$ [%]	ρ [%]	$P_{op.}$ [%]	ρ [%]	$P_{op.}$ [%]	ρ [%]	$P_{op.}$ [%]
$CoFe_2O_4$ (plasma)	82.6	16.0	97.0	0.2	98.5	0.1	97.9	0	-	-
$CoFe_2O_4$ (combust.)	-	-	65.7	34.4	78.3	21.6	93.4	3.1	94.8	2.2
$CoFe_2O_4$ (hydrotherm.)	-	-	81.3	14.2	94.3	0.8	95.0	0.1	-	-
$CoFe_2O_4$ (spray)	-	-	62.3	35.5	90.0	8.8	91.8	4.7	95.1	0.7
$NiFe_2O_4$ (plasma)	87.9	12.1	99.4	0.2	99.8	0.2	100.0	0	-	-
$NiFe_2O_4$ (combust.)	-	-	72.4	25.5	87.7	9.4	96.1	1.6	96.9	1.4
$NiFe_2O_4$ (hydrotherm.)	-	-	69.8	26.7	83.6	14.1	91.4	6.4	-	-
$NiFe_2O_4$ (spray)	-	-	52.2	44.0	69.5	27.6	87.3	10.1	92.7	5.1

ρ – density; $P_{op.}$ – open porosity

Sintering of plasma synthesis products is the fastest of all studied nanopowders: at 900 °C they have high density, but above 1000 °C they are already approach 100% density. $CoFe_2O_4$ ferrite synthesized with other methods has relatively high density after treatment at 1100 °C, but $NiFe_2O_4$ ferrite needed 1200 °C and higher temperatures to reach high density. Although the sintering temperature of ferrites obtained by the spray method is slightly higher, they could be the most technologically advanced of these nanopowders because they are flowing and can be pressed without additional processing.

Crystallite size during sintering grows slightly: from 70-80 nm at 1100 °C up to 120-140 nm at 1300 °C. Grain size of samples obtained from powders by the combustion, hydrothermal or spray method sintered at 1200 °C does not exceed 1-6 µm (Fig. 1). As a result of the high sintering activity of ferrites synthesized in plasma, their grain size is much higher: 10-15 µm for $NiFe_2O_4$ and 10-30 µm for $CoFe_2O_4$.

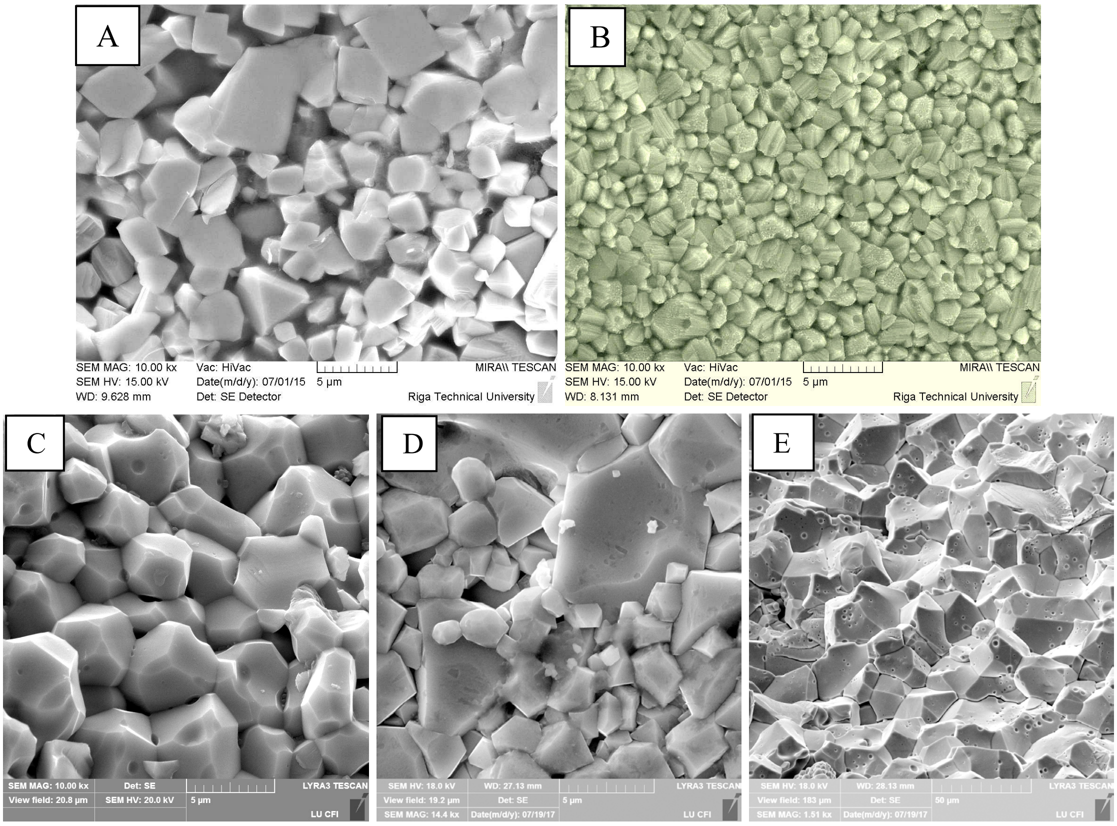

Fig. 1. Typical SEM image of $NiFe_2O_4$ (A, D) and $CoFe_2O_4$ (B, C, E) ceramics sintered at 1200 ºC for 2 h. The powders are prepared by hydrothermal (A, B), sol-gel self-propagating combustion (C), spray-drying (D), and plasma (E) methods

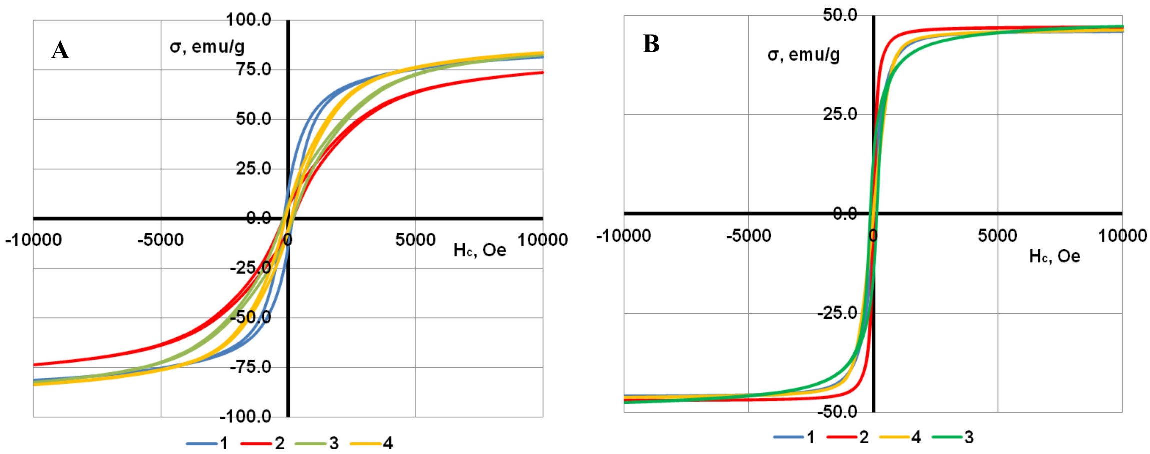

Fig. 2. Magnetic properties of $CoFe_2O_4$ (A) and $NiFe_2O_4$ (B) ferrite sintered at 1200 °C from different powders: 1 – hydrothermal, 2 – spray, 3 – combustion, 4 – plasma

Compared to ferrite nanopowders sintered materials have higher magnetization and lower coercivity (Fig. 2); this can be explained by the increase in grain size and in crystallite size. Increase of sintering temperature will increase the grain size and also increase the magnetization of all ferrite materials, while coercivity will decrease (Table 3). Magnetic properties of samples sintered at 1200 °C are almost the same regardless of production method of ferrite powders: saturation magnetization for $CoFe_2O_4$ is 80-84 emu/g and for $NiFe_2O_4$ – 46-48 emu/g.

Table 3. Magnetic properties of $CoFe_2O_4$ and $NiFe_2O_4$ ceramics after 2 h sintering

Heating temperature [ºC]	$CoFe_2O_4$			$NiFe_2O_4$		
	M_S [emu/g]	M_r [emu/g]	H_c [Oe]	M_S [emu/g]	M_r [emu/g]	H_c [Oe]
Combust.						
1200	82.6	6.9	190	48.2	3.8	20
Hydrothermal						
1100	77.0	20.7	490	42.4	6.5	100
1200	81.3	14.1	170	46.0	1.7	20
Spray						
1100	76.3	8.0	560	47.0	4.2	40
1200	78.3	5.9	190	48.0	3.0	10
Plasma						
1100	81.8	11.1	260	45.7	2.3	40
1200	83.6	6.2	110	46.3	0.7	10

Conclusions

Relatively high density of $CoFe_2O_4$ obtained by combustion, hydrothermal, and spray-drying methods was achieved at 1100 °C, but $NiFe_2O_4$ required 1200 °C or higher temperatures. For these materials sintered at 1200 °C, grain size does not exceed 1-6 µm. Ferrite powders obtained by plasma method are much more active and are sintered at 1000 °C. As a result of intense sintering, the grain size grows sharply: 10-15 µm for $NiFe_2O_4$ and 10-30 µm for $CoFe_2O_4$. Magnetic properties of samples sintered at 1200 °C are almost the same regardless of production method of ferrite powders: saturation magnetization for $CoFe_2O_4$ is 80-84 emu/g, and for $NiFe_2O_4$ it is 46-48 emu/g.

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