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Characterization of Ni ferrites powders prepared by plasma arc discharge process

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ABSTRACT

The aim of this work was to synthesize a single-phase spinel structure from a mixture of zinc, iron and nickel powders by plasma arc discharge method. A mixture of zinc, iron and nickel powders with the appropriate molar ratio was prepared and formed into a cylindrical shape. The synthesis process was performed in air, oxygen and argon atmospheres with the applied arc current of 400 A and pressure of 1 atm. After establishing an arc between the electrodes, the produced powders were collected and their structure and magnetic properties were examined by XRD and VSM, respectively.

ZnO as an impurity was appeared in the as-produced powders owing to the high reactivity of zinc atoms, preventing the formation of Ni–Zn ferrite. A pure spinel structure with the highest saturation magnetization (43.8 emu/g) was observed as zinc powders removed completely from the initial mixture. Morphological evaluations using field emission scanning electron microscopy showed that the mean size of fabricated nanoparticles was in the range 100–200 nm and was dependent on the production conditions.

1. Introduction

In recent years, a considerable attention has been paid to synthesize spinel-type oxides magnetic materials due to their distinctive electrical and magnetic properties, making them desirable for high-frequency applications such as radio frequency circuits, high quality filters, rod antennas, transformer cores, and read/write heads for high speed digital tapes [1–3].

Spinel-type magnetic materials are often denoted by the formula AB_2O_4 where A and B refer to tetrahedral and octahedral sites, respectively, in a network of oxygen ions with FCC arrangement [4]. Ni–Zn ferrite ($Ni_{1-x}Zn_xFe_2O_4$) is one of the cubic spinel ferrites well-known for its remarkable soft magnetic properties, including high magnetic permeability, high electrical resistivity, high Curie temperature and low power loss at high frequencies [5,6].

Up to now, various processes have been developed to prepare nano-sized ferrite particles including sol-gel [7], hydrothermal [8], combustion synthesis [9], chemical co-precipitation [10] and etc. In addition, plasma arc discharge (PAD) method has recently been used to synthesize ultra-fine powders of magnetic oxides [11,12]. Despite all above mentioned methods, PAD is developed to prepare both metal and oxide nanoparticles [12,13]. In this process, nanoparticles are produced immediately after the establishment of the arc between two electrodes by optimizing different parameters such as the arc discharge current, the arc chamber atmosphere, the chamber pressure and etc. [14]. Some of the advantages of this technique are as follows: (a) it is a convenient process which results ultra-fine particle size with high purity, narrow size distribution and well dispersed spherical shape; (b) the physical and chemical properties of the nanoparticles can be easily controlled by varying the processing parameters and no need expensive agents or special equipment; and (c) it has high productive capacity and the high potential for mass production in the industry [15,16].

This method has been used successfully for several metallic materials such as Ni–Cu alloys [15], Mn–Al alloys [17], Cu–Zn alloys [14,18]; and also oxide compounds like Fe_2O_3 [11], NiO [16] and Ni–Mn ferrite–chromite [12]. However, the literature survey shows that soft magnetic ferrites have not been extensively prepared by the PAD method.

The aim of this study is to synthesize a single-phase spinel structure by the PAD method from a specific mixture of Fe, Ni and Zn. Structure and magnetic properties are discussed with respect

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to the arc chamber atmosphere and the electrode composition.

2. Experimental methods

2.1. Materials and preparation techniques

Iron, nickel and zinc powders with a purity of 99% were used as raw material. Stoichiometric amounts of the initial powders, as listed in Table 1, were mixed by using a planetary ball mill at the vial rotation speed of 350 for milling time of 15 min and then introduced into a cylindrical die. Cylindrical bars with diameter of 10 mm and length of 20 mm were prepared under 800 MPa pressure and used as both anode and cathode in arc chamber of the PAD apparatus. According to Table 1, the experiments were performed separately at 1 atm pressures of air, oxygen and argon by the applied electrical current of 400 A. The cathode was connected to the negative pole and the anode connected to the positive pole of a DC current supply. The cathode electrode was fixed and the anode electrode was moved toward the cathode by a DC motor. When the anode reaches to the cathode at a certain distance of about 1 mm, by passing a high current through the electrodes, the arc plasma was formed. The high temperature of the arc, which exceeded 3000 °C [12], caused the electrodes to be vaporized; subsequently, a layer of product powders were deposited on the inner walls of the chamber. After cooling, the powders were collected for characterization.

2.2. Characterization

The phase analysis was performed by the use of X-ray diffraction (XRD, PW-1840 Philips diffractometer with Co Kα1 radiation). The structural parameters including crystallite size and quantitative phase analysis were determined from Rietveld's powder structure refinement analysis of the X-ray powder diffraction data. The Rietveld calculations were performed by the Maud software. This method is based on the using a least squares approach to refine a theoretical line profile until it matches the measured profile. In order to judge the quality of the fitting on the computational diffraction pattern, reliability factor R_{WP} was used. By reducing of R_{WP}, the amount of fitting increased. After achieving a good match, structural parameters were calculated and reported. The morphology and size distribution of the particles were evaluated with the aid of a field emission scanning electron microscope (FESEM). Magnetic properties were measured at room temperature by means of a vibrating sample magnetometer (VSM) with a maximum field of 8 ke at room temperature.

Table 1
Sample coding for different synthesis conditions.

Sample code	Molar ratio: (Fe; Ni; Zn)	Electrical current (A)	Pressure (atm)	atmosphere
$Ni_{0.5}$–O_1I_{400}	(2; 0.5; 0.5)	400	1	Oxygen
$Ni_{0.5}$–Ar_1I_{400}	(2; 0.5; 0.5)	400	1	Argon
$Ni_{0.5}$–A_1I_{400}	(2; 0.5; 0.5)	400	1	Air
$Ni_{0.6}$–A_1I_{400}	(2; 0.6; 0.4)	400	1	Air
$Ni_{0.7}$–A_1I_{400}	(2; 0.7; 0.3)	400	1	Air
$Ni_{0.8}$–A_1I_{400}	(2; 0.8; 0.2)	400	1	Air
$Ni_{0.9}$–A_1I_{400}	(2; 0.9; 0.1)	400	1	Air
Ni_1–A_1I_{400}	(2; 1; 0)	400	1	Air

3. Results and discussions

3.1. The effect of atmosphere

3.1.1. Structure and microstructure

Fig. 1 shows XRD patterns of the as-synthesized powders at the various atmospheres. According to Fig. 1, the characteristic diffraction lines of (Ni, Fe)Fe_2O_4, ZnO and $Fe_{0.72}OZn_{0.13}$ phases are observed in the course of plasma arc discharge for the samples synthesized under air and oxygen atmospheres. Although the above stated phases are clearly evident in their respective X-ray diffraction patterns, their quantitative amounts are different. In order to determine the quantitative phase abundance analysis of the constituent phases at the different atmosphere, the Rietveld's powder structure refinement analysis of the X-ray diffraction data was used. The method is based on a following relation [19]:

$$W_p = \frac{S_p(Z, M, V)_p}{\sum_i^n S_i(Z, M, V)_i} \quad (1)$$

where W_p is the relative weight fraction of phase p in a mixture of n phases, and S, Z, M and V are, respectively, the Rietveld scale factor, the number of formula units per unit cell, the mass of the formula unit (in atomic mass units) and the unit cell volume. Typical graphical pattern obtaining from the Rietveld analysis carried out on the synthesized powders under air atmosphere is illustrated in Fig. 2. The quantitative amount of each phase is shown in Fig. 3. The content of ZnO and $Fe_{0.72}OZn_{0.13}$ phases is different, while both samples include a relatively similar value of (Ni, Fe)Fe_2O_4. Thus, one can deduce that the chemical composition of the synthesized Ni ferrites should be different. Since the characteristic diffraction lines of NiO is not observed in the XRD patterns, Ni ferrites obtained in this study can be described with the general formula $Ni_{0.5+x}Fe_{2.5-x}O_4$ (where $x > 0$). When Ni concentration in the spinel structure of Ni ferrite increases, Fe concentration should be decreased; consequently, more Fe content can be appeared as an impurity. As a result, Ni ferrite synthesized in the oxygen atmosphere due to the high percentage of $Fe_{0.72}OZn_{0.13}$ (33.42wt%) becomes more Ni-concentrated spinel phase. This finding is consistent with the lattice parameter values estimated by the analysis of the X-ray diffraction data (Table 2). The lattice parameter of Ni ferrite shows a decrease in the sample synthesized in the oxygen atmosphere, which can be explained on the basis of the mismatch of ionic radii of Fe^{2+} and Ni^{2+} ions. Since the ionic radius of Ni^{2+} ion (0.78Å) is smaller than that of Fe^{2+} ion (0.83Å) [5], the value of lattice parameter decreases with increasing the value of x.

Appearance of ZnO and $Fe_{0.72}OZn_{0.13}$ phases in the XRD patterns can be ascribed to the presence of Zn in the initial electrodes. Due to the high reactivity of zinc, it melts, evaporates and oxidizes rapidly. In other words, zinc atoms collide with O atom before they can diffuse entirely around Ni and Fe atoms. ZnO phase also appears partly in the X-ray diffraction pattern of $Ni_{0.5}$–Ar_1I_{400} sample, confirming high reaction activity of zinc (Figs. 1 and 3). It should be noted that the trace of ZnO as the main impurity phase was also observed in the other metallic systems in the course of plasma arc discharge [14,20]. With the exception of ZnO, the other identified phases obtained in the inert gas atmosphere are substitutional solid solution or intermetallics compound of Fe–Ni, Ni–Zn and Fe–Zn alloy systems. The quantitative analysis results as well as other structural parameters are listed in Table 3. As listed in this table, crystallite size is found to be in the range 19.8–45.3 nm, confirming nanocrystalline structure of the produced phases.

Fig. 4 shows FESEM photomicrographs of the powders prepared under various atmospheres. The photomicrographs reveal that the powder particles are approximately spherical in shape