Research Article

Effects of Milling Atmosphere and Increasing Sintering Temperature on the Magnetic Properties of Nanocrystalline $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$

Abdollah Hajalilou,¹ Mansor Hashim,¹
Halimah Mohamed Kamari,² and Mohamad Taghi Masoudi³

¹Materials Synthesis and Characterization Laboratory, Institute of Advanced Technology (ITMA),
Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia

²Physics Department, Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia

³Department of Materials Engineering, Islamic Azad University, Najafabad Branch, Isfahan, Iran

Correspondence should be addressed to Abdollah Hajalilou; e.hajalilou@yahoo.com

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Nanocrystalline $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$ was synthesized by milling a powder mixture of Zn, NiO, and Fe_2O_3 in a high-energy ball mill for 30 h under three different atmospheres of air, argon, and oxygen. After sintering the 30 h milled samples at 500°C, the XRD patterns suggested the formation of a single phase of Ni-Zn ferrite. The XRD results indicated the average crystallite sizes to be 15, 14, and 16 nm, respectively, for the 30 h milled samples in air, argon, and oxygen atmospheres sintered at 500°C. From the FeSEM micrographs, the average grain sizes of the mentioned samples were 83, 75, and 105 nm, respectively, which grew to 284, 243, and 302 nm after sintering to 900°C. A density of all the samples increased while a porosity decreased by elevating sintering temperature. The parallel evolution of changes in magnetic properties, due to microstructural variations with changes in the milling atmosphere and sintering temperature in the range of 500–900°C with 100°C increments, is also studied in this work.

1. Introduction

Ni-Zn ferrite is a soft magnetic ceramic that has spinel configuration in terms of a face-centered cubic lattice of the oxygen ions, with the unit cell consisting of 8 f.u. of the type $(\text{Zn}_x\text{Fe}_{1-x})[\text{Ni}_{1-x}\text{Fe}_{1+x}]\text{O}_4$. In this formula the metallic cations in round bracket occupy the tetrahedral A sites and the metallic cations in square bracket occupy the octahedral B sites [1]. Ni-Zn ferrites are important ceramic-magnetic materials in our daily lives due to their extensive use in electrical devices. Due to their unique characteristics such as low eddy current loss, good thermal and chemical stability, and high Curie temperature [2, 3], they are also found in a wide variety of applications. Such applications include being used in microwave devices, rod antennas, power transfer systems, and read/write heads for high speed digital tapes. Several

studies have reported the dependence of magnetic properties of Ni-Zn ferrites on their microstructure, chemical composition, sintering temperature, and preparation method [4–6]. Many researchers, including but not limited to [3, 6–9], have investigated the production of Ni-Zn ferrites via high-energy ball milling as well as the relationship between their magnetic properties, variations in their sintering temperature, composition, and certain other parameters. To the best of our knowledge, no research has been carried out to investigate the effects of a milling atmosphere on the magnetic properties of these ferrites. Therefore, the present study was designed to investigate the effects of milling atmospheres including air, argon, and oxygen on the magnetic properties of Ni-Zn ferrite with the less known composition of $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$ sintered at temperatures ranging from 500 to 900°C.

2. Experimental

Powders of Zn, NiO, and Fe₂O₃ were purchased from Alfa Aesar and used without further purification. These powders were weighed and mixed on the basis of their molar ratios according to the following reaction:

The mixed powders were separately milled in a high-energy ball mill for 30 h under different atmospheres including air, argon, and oxygen. Each of the three types of samples obtained was then mixed with PVA (1%) at a ratio of 1:1. They, then, were dried under an infrared spotlight and pressed into a pellet/toroid form under a load of 4 tons for 7 minutes. Finally, they were subjected to sintering for 2 hours under identical conditions (air atmosphere) at temperatures ranging from 500 to 900°C with 100°C increments at a constant heating rate of 10°C/min.

An X-ray diffractometer (XRD) (Phillips Expert Pro PW3040) using CuK α radiation was used to study the phase changes taking place.

Field emission scanning electron microscopy (FeSEM) using a JEOL JSM-7600F machine was employed to evaluate samples' morphology and microstructure. The average grain size of a sintered body was evaluated over 200 grains using the linear intercept technique. Transmission electron microscopy (TEM) analysis of the samples was carried out by using a 75 kV Hitachi 7100 TEM (Tokyo Japan). The TEM samples were prepared by dispersion of the sintered powders in 95% acetone. In fact, ~0.1 mg of the powders dispersed in 20 mL of acetone and then sonification for 30 min. Eventually, one drop of the suspension was placed on copper TEM grids.

The value of X-ray density was computed based on the suggested equation by Smit and Wijn [10] as follows:

$$\rho_{\text{XRD}} = \frac{8M}{N_a a^3}, \quad (2)$$

where a is the lattice constant, N_a is Avogadro's number (6.02×10^{23}), and M is the molecular weight of the sample. The porosity of the samples was computed based on the following equation:

$$P = \left[1 - \left(\frac{\rho_{\text{exp}}}{\rho_{\text{XRD}}} \right) \right] \times 100\%, \quad (3)$$

where ρ_{XRD} is the X-ray density and ρ_{exp} is the experimental density, which was obtained from the Archimedes Principle.

The magnetic properties of the samples were investigated using a vibrating sample magnetometer (VSM) to attain M - H curves while the maximum field applied was 12 KOe. Samples for the VSM measurement were broken up into small pieces and a mass of 0.03 g was weighed for each sample. Saturation magnetization (M_s) and coercivity (H_c) were determined from the hysteresis loops obtained.

3. Results and Discussion

Figure 1(a) displays the X-ray diffraction patterns of the 30 h milled samples under air, argon, and oxygen atmospheres

FIGURE 1: XRD patterns of (a) the 30 h milled samples under different atmospheres sintered at 500°C and (b) the 30 h milled samples under oxygen atmosphere sintered from 500 to 900°C.

which were sintered at 500°C. Ni-Zn ferrite was formed in all the three samples after sintering at 500°C. It was found that the average crystallite sizes to be 15, 14, and 16 nm, respectively, for the 30 h milled samples in air, argon, and oxygen atmospheres sintered at 500°C. Their sizes increased to 37, 35, and 39 nm after sintering at 900°C, respectively. It is worth mentioning that the crystallite size of Ni-Zn ferrite was calculated by using the XRD patterns and procedures reported in our previous published papers [11, 12]. In Figure 1(b), for example, the XRD patterns of the 30 h milled samples in an oxygen atmosphere sintered from 500 to 900°C are shown. As is evident, by increasing the sintering temperature to 900°C, the width of Ni-Zn ferrite' diffraction peaks decreased and their intensity gradually increased. This indicates the occurrence of crystallite growth during the sintering process. A similar phenomenon was also observed in the two other types of samples milled in the air and oxygen atmospheres sintered from 500 to 900°C.

The TEM and FeSEM images of the 30 h milled samples in different atmospheres sintered at 500°C with their corresponding grain size distribution histograms are shown in Figures 2 and 3, respectively, to better display the effects of milling atmospheres. TEM images showed almost circular ultrafine particles with some agglomerated particles for milled samples in argon atmosphere after sintering at 500°C. The same trait was observed for milled samples in air but with a little bit bigger particles in size. On the other hand, irregular shape with the biggest particles was seen for milled samples

FIGURE 2: TEM images of 30 h milled samples in (a) argon, (b) air, and (c) oxygen atmospheres sintered at 500°C.

in oxygen atmosphere. As an observation, the agglomerated state may be because of the 500°C sintering temperature was not as enough as high to reduce the induced stress during the milling process as well as the existence of magnetic behaviors of particles. The FeSEM images suggest a similar morphology with almost round shaped particles for all three types of atmospheres after sintering at 500°C, but with different grain sizes distribution. It was determined that the grain size distributed in the range of ~30–160 nm in the milled samples in argon atmosphere while the grain size distributed in the range of ~30–170 and 30–190 nm, respectively, in the milled samples in air and oxygen atmospheres. The average grain sizes of the samples milled under air, argon, and oxygen atmospheres sintered at 500°C were 83, 75, and 105 nm, respectively, which grew to 284, 243, and 302 nm after sintering to 900°C. This indicates the dependence of microstructure characteristics on both milling atmospheres and sintering temperatures.

In Figure 4, to further elaborate the effects of the elevated sintering temperature in the milled samples, the FeSEM images of the 30 h milled samples, for example, milled in oxygen, along with their corresponding grain size distribution histograms are shown. These images clearly show an occurrence of grain growth with the increase of the sintering temperature. Sintering temperature at 500°C yielded grain sizes distribution ranging from ~30 nm to 190 nm with an average grain size of 105 nm, dominating grain sizes in the range of 91–101 nm. This indicates that the effect of mechanical alloying to the sintered samples at 500°C was still evident. No remarkable grain growth was observed in the sample which was sintered at 600°C, distributing the grain size in the range of ~50–240 nm with average size of 138 nm. A broader grain size distribution in the range of 80–280 nm with average size of 199 nm was observed for the sample sintered at 700°C. This suggests that the thermal energy provided initiation to affect the grain which grew larger. By increasing sintering temperature to 800°C, as is evident in the FeSEM image for this temperature, small grains connected to larger grains and made dumbbell-like shaped particles. This indicates the starting of a necking process so that the grain size distribution for this sample ranged in 101–370 nm with average size of 224 nm. A broader grain size distribution was observed in the sample which sintered at 900°C as compared to the other sintering temperatures, distributing in the range of ~121–450 nm with an

average size of 302 nm. This reveals that growth to larger grain size accommodated more domain walls development and represented a threshold of the evolution of the bulk ferromagnetic behavior.

According to the presented data in Table 1, it is evident that the density of the samples increased while the porosities decreased by elevating sintering temperature. The reason is due to the fact that during the elevating of the sintering temperature, the occurrence of grain growth causes the porosities segregate to the grain boundaries and the high-densified samples to be obtained [13]. Furthermore, the calculation results revealed that the milled powder in different atmospheres after sintering, at the identical condition, had different density and porosity values. The milled samples under the argon atmosphere possessed the biggest density and lowest porosity. The values of density and porosity were about 4.78 g/cm³ and 6.64%, respectively, after sintering at 500°C. It was determined that their values reached to 4.92 g/cm³ and 3.91% after sintering at 900°C. The milled samples under the oxygen atmosphere had the smallest value of density with about 4.85 g/cm³ and highest porosity about 5.46% after sintering at 900°C. Since the 900°C sintering temperature is not higher, the obtained higher densification can be associated with the homogenous distribution of fine particles at the packed structure and the use of Zn instead ZnO in the initial reactants.

It is well known that two sources cause a porosity generation in ceramic materials, intergranular porosity (P_{inter}) and intragranular porosity (P_{intra}). The total porosity can be expressed as $P = P_{\text{inter}} + P_{\text{intra}}$. The intragranular porosity (P_{intra}) strongly is dependent on the grain size [14]. Consequently, it can be induced that the enhancement of intragranular porosity (P_{intra}) induces from discontinuous grain growth. The grain sizes present the essential effect on the domain wall's contribution in the magnetization at low frequency. At the higher rate of grain growth, the rapid movement of the grain boundaries causes the pores to be left behind and trapped inside the grains. In practice, it is difficult completely to remove intragranular pores which are causing poor magnetic properties. By elevating the sintering temperature, a generated force of thermal energy drives the grain's boundaries to grow over pores, resulting in the densifying of material and reducing the pore volume. The discontinuous

FIGURE 3: FeSEM images of 30 h milled samples in (a) argon, (b) air, and (c) oxygen atmospheres sintered at 500°C with their corresponding grain size distribution histograms.

TABLE 1: Lattice parameter, theoretical density, experimental density, porosity, and grain size for milled samples in air, argon, and oxygen atmospheres sintered in the range temperature of 500–900°C.

Mill atmosphere	Sintering temperature (°C)	Lattice parameter (Å)	Theoretical density (X-ray density) (g/cm ³), ρ_{xrd}	Experimental density (g/cm ³), ρ_{exp}	Porosity (%) $[1 - (\rho_{\text{exp}}/\rho_{\text{xrd}})] \times 100\%$	Grain size (μm)
Argon	500	8.4023	5.12	4.78	6.64	0.075
	600	8.4030	5.12	4.80	6.25	0.110
	700	8.4016	5.12	4.85	5.27	0.161
	800	8.3998	5.12	4.88	4.69	0.195
	900	8.4025	5.12	4.92	3.91	0.243
Air	500	8.4086	5.12	4.72	7.81	0.083
	600	8.4027	5.12	4.76	7.03	0.127
	700	8.4022	5.12	4.79	6.44	0.176
	800	8.4025	5.12	4.84	5.47	0.211
	900	8.4031	5.12	4.90	4.30	0.284
Oxygen	500	8.3813	5.15	4.68	9.13	0.105
	600	8.3885	5.14	4.74	7.78	0.138
	700	8.3945	5.14	4.79	6.81	0.199
	800	8.3959	5.14	4.81	6.42	0.224
	900	8.3948	5.13	4.85	5.46	0.302

grain growth leads to the hindrance of the pores to the grain boundaries' migration, thus, contributing to the density reduction.

Generally, the calculated values of densities are approximately 97% of the theoretical density of the materials (5.13 g/cm³). These results have confirmed that the mechanical alloying is thriving in powder compaction to obtain close to theoretical density. On the other hand, the porosity would reduce by elevating sintering temperature which is good agreement with the well mentioned phenomena [15].

Figure 5 displays the room temperature M - H hysteresis loop of the samples milled for 30 h under argon, oxygen, and air atmospheres which sintered at temperatures from 500 to 900°C. As reported in our previous work [11], by investigation of the effect of milling atmosphere on the Ni-Zn ferrite magnetic properties, it was found that the 30 h milled samples in different atmospheres had S-like hysteresis curves with very low coercivity and small average particle sizes. These are the characteristics of superparamagnetic materials according to [11, 16]. Therefore, the Langevin equation was used to nonlinear least fitting of the initial magnetization curves of the milled samples, and expressed as

$$M(H) = M_s \left[\coth\left(\frac{\mu H}{K_B T}\right) - \left(\frac{K_B T}{\mu H}\right) \right], \quad (4)$$

where M_s , $M(H)$, T , K_B , and m denote the saturation magnetization, the magnetization for an applied field H , the absolute temperature, Boltzmann's constant, and the uncompensated magnetic moment, respectively [17]. The M_s values for the 30 h milling samples in argon, air, and oxygen are estimated to be about 5.33, 4.53, and 3.44 emu/g, respectively.

Figure 6 shows the respective correspondences between saturation magnetization and sintering temperature, density,

grain size, and porosity for the samples milled for 30 h under air, argon, and oxygen which were sintered from 500 to 900°C under identical conditions. The increasing saturation magnetization of the samples indicates that the sintering process significantly improves magnetic properties. The sintering of the 30 h milled samples at a temperature range of 500–900°C increased saturation magnetization from 4.53, 5.33, and 3.44 (for the samples milled for 30 h under air, argon, and oxygen, resp.) to 54.5, 58.9, and 50.5 emu/g at $T = 900^\circ\text{C}$. This is because of the canted spin configuration induced by the ball milling process, the distribution of nonequilibrium cations, and their relaxation towards the equilibrium arrangement [18]. In fact, the sintering process leads to the relaxation of the mechanically produced Ni-Zn ferrite towards a magnetic and structural condition.

The M - H curves indicate the dependence of saturation magnetization on increasing sintering temperature. The relationship for temperature in the range of 500–900°C can be expressed by (5) as follows [19]:

$$M_s = 8.1661 \exp\left(\frac{3T}{1000}\right), \quad (5)$$

where T is temperature. The enhancement of M_s by elevating sintering temperature may be associated with the reduced volume fraction of grain boundaries (increasing grain size) as well as the decline of the induced lattice strain during the milling process and the solid-state diffusion of the remaining oxides into the spinel ferrite lattice structure. In nanostructured materials, the grain boundaries and the surface of the particles, which possess a higher energy compared to the lattice, play a key role in the determination of their magnetic behavior so that the ground-state magnetic configuration of the atoms placed in the surface or interface regions differs from those corresponding to bulk materials [19].

FIGURE 4: FeSEM images of 30 h milled samples in oxygen atmospheres which sintered from 500°C to 900°C.

The increase in M_s with increasing grain size and the decrease in M_s with increasing porosity indicate that M_s strongly depends on microstructural characteristics such that they are influenced by increased sintering temperature. This is expressed by the following equation reported by Greneche and Ślowska-Waniewska [19]:

$$M_s = (\partial s \rho) (1 - P), \quad (6)$$

where ∂s is the M_s (obs.)/ M_s (sat.), ρ is the experimental density, and P is the porosity. Obviously, M_s is inversely

proportional to porosity. The reason for the reduction in M_s with increasing porosity is that the divalent ions of iron possess more magnetic neighbors due to the high number of zinc cations, whereby the spins become coupled. The magnetic moment modification with Zn concentration may be described on the basis of Yafet-Kittel type spin configuration [20].

However, the relationship between M_s and density of the samples sintered from 500 to 900°C suggests that M_s enhances with increasing density in the samples milled in

FIGURE 5: Room temperature M - H hysteresis loops of $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$ ferrite powders activated for 30 h in different atmospheres and sintered from 500°C to 900°C.

different atmospheres. Consequently, it may be concluded that M_s has directly proportional to density in samples milled under air, argon, and oxygen atmospheres. This is because the spin movement is facilitated by increasing density. Furthermore, the number of pores reduces as a result of elevating sintering temperature since they act as barriers to wall motion.

The following equation [21] was used to calculate a magnetic moment (n_B) for the mentioned samples and the results were reported in Table 2:

$$n_B = \frac{(\text{Mol.Wt.}) \times (M_s)}{5585}, \quad (7)$$

where 5585 is the magnetic factor.

As is evident in Table 2, the magnetic moment increased with increasing sintering temperature. Furthermore, samples milled in different atmospheres exhibited different values of a magnetic moment so that the values for those milled under air, argon, and oxygen were 2.235 (emu/g), 2.415 (emu/g), and 2.071 (emu/g) after sintering at 900°C, respectively. This indicates the variations in the magnetic properties as a result of changes in temperature and microstructure.

Comparing the M_s value of Ni-Zn ferrite produced in this study with those of the literature, that is, solid reaction (48.5 emu/g) [22], SHS (66.2 emu/g) [23], and wet chemical (45.5 emu/g) [24], indicates that the magnetic properties of Ni-Zn ferrite strongly depends on the preparation method and the heating temperature. However, the M_s values for

TABLE 2: The values of M_s and n_B with the elevating sintering temperature in the samples milled under different atmospheres.

Mill atmosphere	Magnetic parameters	30 h milled	500°C	600°C	700°C	800°C	900°C
Air	M_s (emu/g)	4.53	21.2	29	39.4	53	54.5
	n_B (emu/g)	0.186	0.869	1.189	1.615	2.173	2.235
Argon	M_s (emu/g)	5.33	23	36	47.5	56.14	58.9
	n_B (emu/g)	0.218	0.943	1.476	1.948	2.302	2.415
Oxygen	M_s (emu/g)	3.44	19	26.5	40	46.3	50.5
	n_B (emu/g)	0.141	0.779	1.086	1.640	1.898	2.071

FIGURE 6: Relations between M_s and sintering temperature, grain size, porosity, and density in the $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$ ferrite.

the samples sintered above 800°C possess a higher value; totally, their M_s values are much lower as compared to the other preparation methods. The relative low value of magnetization in the milled-sintered samples may be due to the different factors, such as very small crystallite size, the remaining initial oxides, and lattice defects and strains induced during the milling process. The strains in fine particles produced by

the ball milling affect the overall magnetization (probably due to an increase in surface spins) because of displacement of ions and disordering. After sintering, the magnetization is considerably increased as a result of lattice strain as well as crystal defects reduction in the sintered samples.

The other reason for a lower M_s obtained is due to the fact that the lower sintering range temperatures of 500–900°C were

FIGURE 7: Coercivity versus sintering temperature from 500 to 900°C for $\text{Ni}_{0.36}\text{Zn}_{0.64}\text{Fe}_2\text{O}_4$ ferrite.

not enough high to cause the relaxation of nonequilibrium cation distribution and the canted spin arrangement resulting from the mechanical alloying towards the equilibrium configuration.

Figure 7 presents the variation in coercivity as a function of sintering temperature. The variation of coercivity as a function of sintering temperature is consistent with the changes in both density and grain size. This can be explained on the basis of crystal anisotropy, diameter of particles, and domain structure. Elevating the sintering temperature leads to these variations due to the transformation or decomposition of the phases. This, in turn, causes changes in the size, shape, and number of the pores while the grain size is also enhanced. The as-received materials, being nanosized, are not likely to possess any grain boundaries; but the sintering process would influence grain boundaries as well as some microstructural imperfections. However, increased sintering temperature leads to reduced number of lattice defects such as grain boundaries and dislocations, which gives rise to reduced coercivity. In other words, grain growth occurred by the grain boundary migration during the sintering process. As grains enlarge in size, the total grain boundary area reduces, submitting an attendant reduction in the total energy, which is the driving force of grain growth [25]. In terms of the coherent polycrystal model [26], the volume fraction of the grain boundaries (f_{gb}) can be evaluated by the following equation:

$$f_{\text{gb}} = 1 - \frac{(D-d)^3}{D^3}, \quad (8)$$

where d is the effective grain boundary thickness, which comprises 2, 3 atomic layers [27] and D is the average grain size. Interplanar spacing for the (3 1 1) set of planes is assumed here to estimate the effective grain boundary thickness. Accordingly, the volume fraction of the grain boundaries, that is, the milled samples in the argon atmosphere, decreases from 32.5% at room temperature to 3.9% at 900°C.

It has been stated that, according to the well-accepted $1/D$ law, coercivity would reduce with increasing grain size in large-grained polycrystalline soft magnetic materials [28].

With respect to Herzer's random anisotropy model [29], grain size has a fundamental effect on coercivity. Based on the D^6 law, coercivity tends to decline sharply with a reduction in grain size in the case of grain sizes smaller than the length of magnetic exchange (i.e., $L_{\text{exch}} \sim 40\text{--}50\text{ nm}$).

The 30 h milled samples exhibited the highest coercivity as compared to after sintering. The reason may lie in the residual strain induced during the milling process and the small crystallite size.

In brief, the changes in the coercivity values, for the samples milled under air, argon, and oxygen atmospheres and sintered from 500 to 900°C, may be classified into three steps. In the early step, coercivity remarkably reduced from 87, 89.2, and 53.5 Oe at room temperature to 23.5, 24.7, and 22.85 Oe at 500°C, respectively. In a second step, the values rose to 41.13, 45 and 40.7, and 41.13 Oe with a slight fluctuation between 550 and 800°C. Finally, they declined to 26.6, 31.42, and 28.56 Oe at sintering temperatures between 800 and 900°C.

Herzer's random anisotropy and the classic models were used to explain the variations in the values of coercivity with respect to the size of the crystalline. In none of the three samples, did coercivity obey Herzer's random anisotropy model ($H_c \propto D^6$). The reason for this unexpected behavior might lie in the residual stress induced during the milling process or in the high densities of the structural imperfections. Since this model cannot capture the influence of residual stress, it cannot be applied for the milled powder, either. As it was not possible to avoid residual stresses during the milling process, Shen et al. modified Herzer's random anisotropy model to account for the effects [30]. According to this modified version, the creation of lattice imperfections, like dislocations, contributes mainly to the residual stresses during the milling process. In this way, the model predicts that coercivity in the case of $D < L_{\text{exch}}$ in the milled nanocrystalline magnetic materials depends on both crystallite size and dislocation density (residual stress). The proposed model can be articulated as follows:

State 1: $|M_s| \rightarrow 0$, Dislocation $\rightarrow 0$, $H_c \propto d^6$.

State 2: $|M_s| \rightarrow 0$, Dislocation $\gg 0$, $H_c \propto d^6$.

State 3: $|M_s| \gg 0$, Dislocation $\rightarrow 0$, $H_c \propto d^6$.

State 4: $|M_s| \gg 0$, Dislocation $\gg 0$, $H_c \propto d^{1/2}$.

This model provides a proper explanation for the reduced coercivity at the early step of preparing all the samples. According to this explanation, the decline of coercivity as a result of sintering at low temperatures (first step) indicates that the lattice imperfections were eliminated and that the relaxation of residual stress was dominant. In the second stage, however, the lattice strain had a downward trend in all the samples after sintering at 600°C while coercivity took an upward trend. The reason can be ascribed to the increase in crystallite size as described by Herzer's random anisotropy model.

After sintering at 800 to 900°C (the third step), coercivity dropped to 26.6, 31.42, and 28.56 Oe in the samples milled under air, argon, and oxygen, respectively. This is elucidated on the basis of the classic model ($H_c \propto 1/d$). It has been

FIGURE 8: The effects of grain size on coercivity in the samples sintered from 500 to 900°C.

stated that grain boundaries are the most crucial factors contributing to coercivity in the case of large-grained polycrystalline nanomaterials ($d > L_{\text{exch}}$). Therefore, fine-grained soft magnetic materials are often magnetically harder than coarse-grained soft ones with identical compositions. As a result, coercivity would have a tendency to decline since the grain size increases, according to the well-accepted $1/d$ law [28]. Figure 8 displays the effect of grain size on coercivity in the samples sintered at 500–900°C.

Goldman (1999) found that the coercivity of soft magnetic materials is sensitive to microstructural characteristics such as grain size, porosity, and anisotropy [31]. Pal et al. [32] reported high coercivity in soft spinel ferrite materials with nanosized dimensions as compared to that in micron-sized ones. Inui and Ogasawara [33] found the inverse proportion of coercivity to grain size in multidomain grains. This is because the enlargement of the grains takes place with increasing sintering temperature in such a way that the larger grains contain more domain walls, enhancing the wall movement contribution to magnetization or demagnetization [33, 34]. In fact, wall movement requires a lower energy than the rotation of domains. Consequently, a lower coercivity is expected in large grains [33]. On the other hand, according to Ladislaus [35] and George et al. [36], a single-domain state dominates below a critical grain size and H_c reaches its maximum value in the range of critical grain size. A careful examination of Figure 8 reveals that H_c had an upward trend with grain growth until a certain region of grain size and, after that, a sharp reduction occurred in the H_c value. This up-down trend variation in the H_c value with grain growth was considered critical to grain size for Ni-Zn ferrite samples. However, a critical grain size value was different for milled samples in different atmospheres so that its value was 0.195, 0.211, and 0.224 μm, respectively, for 30 h milled samples under the argon, air, and oxygen atmospheres sintered from 500–900°C under the same conditions. This indicates that the value of coercivity depends on the critical grain size and the milling atmosphere. It was found that coercivity increased in all the samples with grain sizes below the critical value and at

temperatures below 800°C. This can be explained on the basis of magnetocrystalline and shape anisotropy factors. Above 800°C and beyond a critical grain size, the shape anisotropy factor would diminish and the magnetocrystalline would be the dominant factor. Furthermore, above a critical grain size, coercivity would be controlled through anisotropy and defects, such as pores.

4. Conclusion

High-energy ball milling with subsequent heat treatment was used to produce the single phase of Ni-Zn ferrite nanocrystalline. It was found that the milling atmosphere played a key role in the magnetic properties of the ferrite, such that the samples milled under argon exhibited a high saturation magnetization as compared to the other two samples. Increasing sintering temperature from 500°C to 900°C resulted in grain growth in all the three types of samples but the grain size of the milled samples under oxygen atmosphere was remarkably bigger than the two others. It also resulted in increase of density and decrease of porosity in all the samples, which led to the development of magnetic properties such as increased saturation magnetization. Coercivity exhibited some fluctuation in all the three types of samples. The classic model and the modified random anisotropy model were used to explain these phenomena.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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