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Microstructure and magnetic characteristics of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite synthesized by a spraying–coprecipitation method*

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Nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite with average grain sizes ranging from 10 to 100 nm is prepared by using a spraying–coprecipitation method. The results indicate that the nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite is ferromagnetic without the superparamagnetic phenomenon observed at room temperature. Specific saturation magnetization of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite increases from 40.2 to 75.6 emu/g as grain size increases from 11 to 94nm. Coercivity of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite increases monotonically when $d < 62$ nm.The relationship between the coercivity and the mean grain size is well fitted into a relation $H_c \sim d^3$. A theoretically evaluated value of the critical grain size is 141nm larger than the experimental value 62nm for nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite. The magnetic behaviour of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite may be explained by using the random anisotropy theory.

Keywords: nanocrystalline material, $Ni_{0.5}Zn_{0.5}$ ferrite, spraying–coprecipitation method, magnetic properties

PACC: 7530G, 7560J, 7550D

1. Introduction

The magnetism of nanoscopic systems has drawn much attention due to the unique magnetic properties and the technological applications of such systems.[1,2] As is well known, the magnetic properties of solid are very sensitive to their microstructures. By varying the grain size of a material from a micron to nanometre scales, its magnetic structure will change from a multidomain to a single domain configuration. Accordingly, the magnetization process will evolve from domain wall motion to the mechanism of magnetization rotation, which can lead its coercivity to increase.[3] Thus, in order to obtain excellent performances for soft magnetic materials, the conventional method is to make grain size as large as possible. However, recent studies[4−8] have demonstrated that as the grain size is much smaller than the single domain particle or domain wall size, random anisotropy may be dominant, which leads to a considerable reduction in magnetocrystalline anisotropy, resulting in both very low coercivity and high permeability. In other words, its magnetic behaviour can be controlled by using the nano-processing, so one can obtain a higher saturation magnetization and permeability at no expense of the other magnetic performances. Therefore, the nano-processing seems to be a potential and promising measure to improve the magnetic properties of the soft magnetic materials.

Nickel–zinc (Ni–Zn) ferrite is one of the most versatile soft magnetic materials, and it has been used in high-power device and high-frequency cases, such as transformers and telecommunication applications.[9] Especially, $Ni_{0.5}Zn_{0.5}$ ferrite has been noted to have a low magnetic coercivity, large permeability, remarkably high electrical resistivity and low eddy current loss. However, these properties are sensitive to the compositions, microstructure and heat treatment. Therefore, it is important to obtain high pure and ultrafine Ni–Zn ferrite powders in order to be able to achieve its high properties. Recently, nanocrystalline Ni-Zn ferrite powders have been synthesized by using various techniques such as mechanical attrition,[10] hydrothermal method,[11] sol-gel method,[12] combustion synthesis process,[13] etc. In the present paper, nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite powders are synthesized by a modified wet chemical method called spraying–coprecipitation process. Microstructure of

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nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite is investigated, and the effect of the grain size on magnetic properties of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite is also discussed.

2. Experimental procedure

$Ni_{0.5}Zn_{0.5}$ ferrite nanoparticles were prepared by using the spraying–coprecipitation method in the present paper. Namely, reagent grade nickel chloride, zinc chloride and iron chloride with a content ratio were first dissolved in a jar. These metal ions and the sodium hydroxide solution were transferred and sprayed into a flask by using the pressurized nitrogen (Fig.1). The mixture was stirred to obtain the precipitates, then they were washed several times with distilled water and dried at about 100°C for 24h. The precursors obtained were calcined at several different temperatures so as to form the spinel phase and alter its grain size.

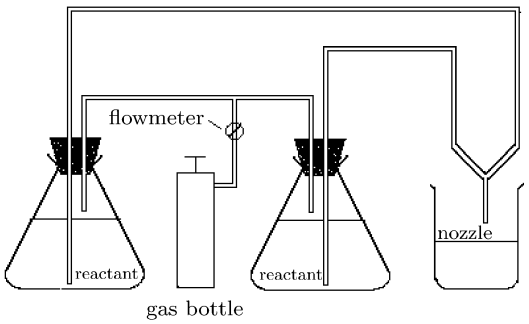


Fig.1. Schematic diagram showing spraying-coprecipitation method.

X-ray diffraction (XRD) was performed in a 2θ range of 10°–90° on Thermo Electron ARL X′ TRA with Cu–Kα radiation. Mean grain size was evaluated based on the Scherrer formula. The main constituent elements were determined by energy dispersive x-ray spectroscopy (EDS) equipped with a scanning electron microscope (SEM). Microstructural characteristics were further confirmed by transmission electron microscope (TEM). The specific surface area of the sample was determined by using the Brunauer–Emmett–Teller (BET) method with nitrogen adsorption. Differential scanning calorimetry and thermogravimetric (DSC-TG) measurements were carried out on a Netzsch STA 449C with 10°C/min in air atmosphere. Magnetization measurements were performed with a LakeShore 7307-9309 vibrating sample magnetometer (VSM) at room temperature.

3. Results

3.1. DSC-TG analysis

DSC-TG curves of precursor are shown in Fig.2. Firstly, a consecutive weight loss occurs below 200 °C, which is attributed to the loss of water. Then a further slight weight loss takes place at temperatures in a range of 200 − 320 °C, which is due to the decomposition of the precursor. With temperature further increasing, there appear two exothermic peaks P_1 and P_2 centred at 390 °C and 660 °C, respectively. XRD pattern verifies the formation of spinel phase calcined at 300 °C, which is indicated by exothermic peak P_1 that can be ascribed to the formation of $Ni_{0.5}Zn_{0.5}$ ferrite. Meanwhile, XRD patterns also indicate that the formation of $Ni_{0.5}Zn_{0.5}$ ferrite is not complete when calcining temperature is below 300 °C. Therefore it can be deduced that the exothermic peak P_2 is closely related to the further grain growth of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite.

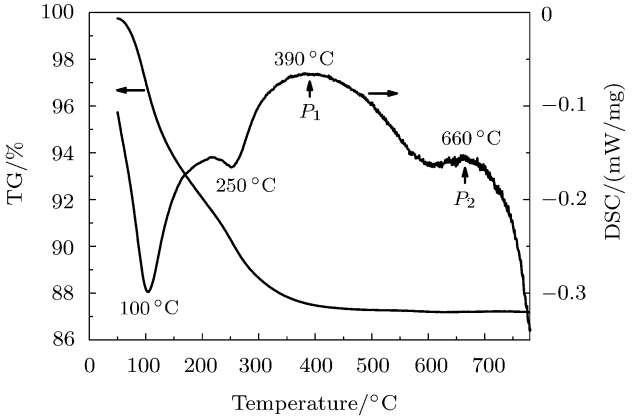


Fig.2. DSC-TG plots of $Ni_{0.5}Zn_{0.5}$ ferrite precursor.

3.2. Crystal structure and grain size

Figure 3 shows the XRD patterns of specimens calcined at different temperatures. It can be seen that all diffraction peaks are identified to be due to a spinel (fcc) crystalline structure, No any other phases are detected on these specimens. With the increase of calcining temperature, the main features of XRD patterns do not change, except for the sharpening of the reflection peaks. This sharping of the reflection peaks reveals the grain growth of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite in the calcining process. From the widths of the three reflection peaks (220), (311) and (400), the average grain sizes of specimens are obtained. Table 1

shows the variation of the average grain size d_m of the specimen with calcining temperature. One can observe that the crystallites have a size in a nanometre range and their mean diameter increases with temperature. At temperatures below 700 °C, the specimen with an average grain size smaller than 32nm can be obtained.

Table 1. The average grain size of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite as a function of temperature.

Temperature/°C	300	400	500	600	700	750	850	950	1050
d_m/nm	9.5	10.7	15.8	22.3	31.7	40.7	62.0	83.3	94.0

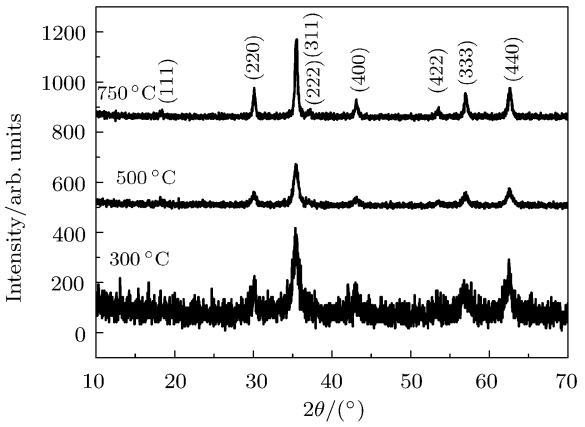


Fig.3. XRD patterns of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite calcined at different temperatures.

Figure 4 shows a typical TEM image of specimen calcined at the temperature of 600 °C for 1.5h. It can be seen that: (i) most of the grains are of an approximately spherical shape; (ii) the grain sizes of specimen are around 30 nm, which is consistent with XRD analysis results; (iii) a few of large agglomerate particles (about 100 nm) are present, which is ascribed to the intense surface effect of nanosized materials in order to minimize its magnetostatic energy and surface energy.

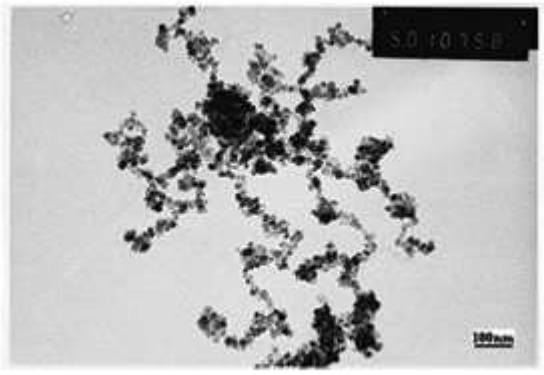


Fig.4. TEM of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite calcined at 600 °C for 1.5h.

Figure 5 gives the specific surface area of specimen as a function of temperature. One can see that the specific surface of specimen decreases from 124.8 to 1.06 m^2/g as calcining temperature increased from 300 to 1050 °C. Corresponding to this change, the agglomerate particle size of specimen increases rapidly from 9 to 1061 nm using the BET analyser.

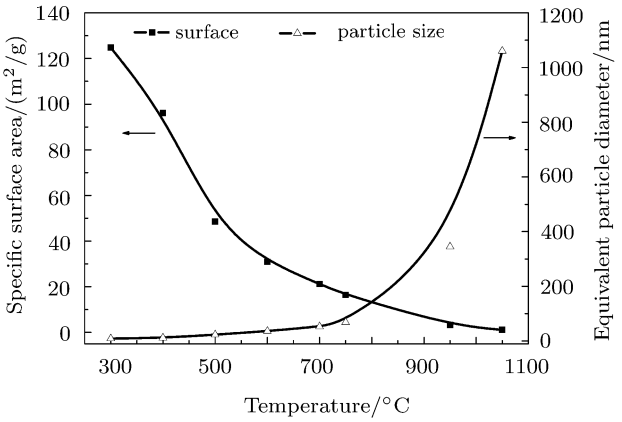


Fig.5. Specific surface area and equivalent particle size of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite calcined versus temperatures.

3.3. Magnetic properties

Figure 6 shows hysteresis loops of specimens at room temperature. No any other superparamagnetic phenomena are observed in specimens. Magnetization nearly reaches saturation at an external field of ∼300 kA/m. With external field increasing to 800 kA/m, it becomes completely saturated. Table 2 shows the variations of specific saturation magnetization M_s and coercivity H_c of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite with calcining temperature. It can be seen that the specific saturation magnetization increases from 40.2 to 75.6 emu/g as calcining temperature increases from 400 to 1050 °C. Corresponding to this change, coercivity increases with grain size,

and the maximum coercivity is 5.97 kA/m as calcining temperature reaches 850 °C, which means that the experimental critical grain size of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite is around 62 nm. Then coercivity decreases with temperature.

Table 2. Magnetic properties of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite calcined at different temperatures.

Temperature/°C	400	500	600	700	750	850	950	1050
M_s/(emu/g)	40.2	40.7	48.1	66.8	71.8	73.1	73.5	75.6
H_C/(kA/m)	1.08	1.16	2.77	4.69	5.06	5.97	4.30	2.04

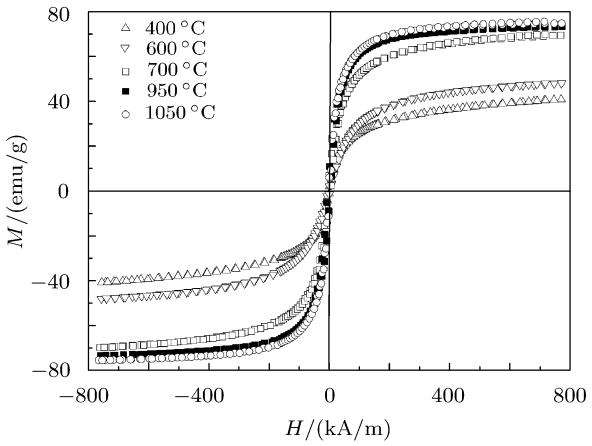


Fig.6. Hysteresis loops of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite at room temperature.

4. Discussion

4.1. Saturation magnetization

When the crystalline size decreases to a nanometre range, there occur three factors that become important: volume effect, surface atom effect and shape anisotropy effect. These factors have significant effects on magnetic properties. In our experiment, the decrease of the specific saturation magnetization M_s with the decrease of the nanocrystallite dimension may originate from the surface effects that are due to finite-size scaling of nanocrystallites, which in turn leads to a non-collinearity of magnetic moments on their surface.[14−16] Surface effects account for the fact that the specific saturation magnetization of the nanocrystallite system is lower than that of coarse-grained $Ni_{0.5}Zn_{0.5}$ ferrite.

4.2. Effect of grain size on coercivity

It is well known that good soft magnetic characteristics including higher saturation magnetization and lower coercivity are obtained when the domain wall motion or domain rotation occurs with a small change in the energy of the system. One factor that may strongly affect the energy of the system is magnetic anisotropy. The intrinsic material parameters that dominate the amplitude of the magnetocrystalline energy in nanostructured magnetic materials include the grain size d, the magnetocrystalline anisotropy constant K_1 and the exchange stiffness constant A. Recently, the theory of random anisotropy model and experiments show that when $d < d_0$, a relation exists between coercivity and the grains size, i.e.

$$H_c \sim d^N, \tag{1}$$

where d_0 is the critical grain size, and N is a constant. This critical size is determined by ferromagnetic exchange length L_{ex} as follows:

$$d_0 \approx L_{ex} = (A/K_1)^{1/2}, \tag{2}$$

In order to compare the present experimental results with the results from this theory, first we evaluate the exchange length L_{ex} for nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite. Exchange stiffness constant A is related to exchange integral J by the formula[17]

$$A = nJS^2/a, \tag{3}$$

where n is the number of atom in a primitive cell (for spinel structure $n = 4$), S is the total spin of electrons, and a is the lattice constant. According to curie point T_c and crystalline structure of $Ni_{0.5}Zn_{0.5}$ ferrite, the following approximation relation may be used:[18]

$$J \approx 0.15T_c. \tag{4}$$

In addition, we cite values of lattice constant a from Ref.[19], Curie temperature T_c from Ref.[20], magneto-crystalline anisotropy constant K_1 and total spin of electrons S of $Ni_{0.5}Zn_{0.5}$ ferrite from Ref.[21]. Therefore, the exchange stiffness and exchange length of $Ni_{0.5}Zn_{0.5}$ ferrite can be calculated

based on Eqs.(2), (3) and (4). Table 3 lists the calculated results. The theoretically evaluated exchange length L_{ex} is around 141nm for $Ni_{0.5}Zn_{0.5}$ ferrite. Comparing the critical grain size (62 nm) of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite with theoretically evaluated exchange length, one can see that the exchange length is 2.27 time greater than the critical grain size for nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite. This means that the random anisotropy should happen, and the coercivity should decrease when the grain size of $Ni_{0.5}Zn_{0.5}$ ferrite is smaller than 141 nm.

Table 3. List of lattice constant a, Curie temperature T_c, crystalline anisotropy constant K_1, exchange stiffness A and exchange length L_{ex} of $Ni_{0.5}Zn_{0.5}$ ferrite.

a/Å	T_c/K	$K_1/(10^3 J/m^3)$	S	$A/(10^{-12}$ J/m)	L_{ex}/nm
8.38	550	1.7	5/2	21.75	141

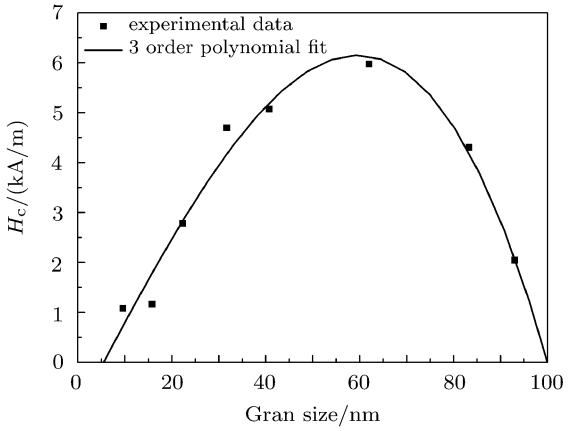


Fig.7. Coercivity of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite versus average grain size.

Figure 7 shows the variation of the coercivity versus grain size. It can be seen that it is well fitted into a relation $H_c \sim d^3$, implying that the random anisotropy can function effectively. One can see that the fitting curve of the grain size dependence of coervicity has a lower value of ferromagnetic exchange length L_{ex} of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite than the one calculated according to Eq. (2). The reason why there occurs such a discrepancy may be due to the fact that a simple random anisotropy model has been used in the calculation: the model does not take into consideration the particle shape, particle-size distribution and the interaction between particles that are closely related to the value of L_{ex}. Furthermore, in the case of nanoscale particles the surface effects may not be neglected. Taking into account all these factors, the constant for magnetocrystalline anisotropy can be corrected, and it may be replaced with the constant of effective anisotropy K_{eff}[1,5,22]

$$K_{eff} = K_1 + K_{sh} + K_s + K_{int}, \qquad (5)$$

where K_{sh} is the constant of shape anisotropy, K_s is the constant of surface anisotropy, K_{int} is the constant of supplementary anisotropy that indicates nanocrystalline interactions. Taking into account all these considerations, the experimental value of the critical diameter of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite being lower than the theoretical value is justified. Further theoretical analysis based on magnetocrystalline anisotropy is necessary.

5. Conclusion

Nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite is prepared by a spraying–coprecipitation method. Microstructures and magnetic properties are investigated. The following conclusions can be drawn:

(1) Magnetic measurement shows that the nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite with average grain sizes ranging from 10 nm to 100 nm is ferromagnetic; no any other superparamagnetic phenomena are observed in samples at room temperature.

(2) The specific saturation magnetization increases from 40.2 to 75.6 emu/g with grain size as the calcining temperature increases from 400 °C to 1050 °C.

(3) The magnetic behaviour of nanocrystalline $Ni_{0.5}Zn_{0.5}$ ferrite is well consistent with that from the random anisotropy theory. When grain size is smaller than 62 nm, the coercivity decreases with grain size, obeying the law $H_c \sim d^3$ well.

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