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Effect of annealing on the magnetic behavior and microstructures of spherical NiZn ferrite particle prepared by ultrasonic spray pyrolysis

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Abstract The spherical NiZn ferrite particles were prepared by ultrasonic spray pyrolysis with mixed solution of aqueous metal nitrates. The NiZn ferrite particle was observed with nano-sized primary particles of about 10 nm or less before annealing which represented as paramagnetic behavior measured at 77 K and room temperature. The typical abnormal growth of primary particles like polyhedral primary particles was observed by annealing at 1273 K with Zn-concentration dependency. The XRD patterns showed good crystallinity of NiZn ferrite powder after annealing. In annealing process, the intra-particle sintering phenomenon was observed and the spherical particle morphology was collapsed at 1673 K. The saturation magnetization of NiZn ferrite powder for each annealing temperature was decreased with measuring temperature of 77~300 K.

Key words Spherical particle, NiZn ferrite, Ultrasonic spray pyrolysis

1. Introduction

In synthesizing multi-component ceramic powders, it is difficult to obtain the single phase and homogeneous composition material and to condense several reactants simultaneously from their vapors in the desired stoichiometry. The powders synthesized by the spray pyrolysis method are more uniform in composition than those produced by many other techniques because the reaction is confined to micro-sized droplets. Phase segregation may also occur with the spray pyrolysis of multicomponent materials because of the different solubilities of the precursor components, even though it occurs in droplets [1]. The spray pyrolysis processing is generally to use mixed nitrates of each component as precursors. Spray pyrolysis decomposition is normally a valuable technique to form nonagglomerated complex mixed metal oxide powders with high purity, crystallinity, and relatively narrow particle size distribution [2].

Polycrystalline ferrites have been used widely in many electronic devices because of its various electrical and magnetic characteristics in applications. NiZn ferrite has the attractive properties of high Curie point, high resistivity and low-dielectric loss constant. In recent years, nano-sturctured materials were intensively studied both theoretically and experimentally, due to the new properties compared to the bulk material. Nano-structured materials can be obtained both by physical and chemical method [3-6]. However, chemical methods are applied more often due to its advantages such as homogeneity, high purity, low cost and efficiency. Since the spinel ferrite is especially interesting in the properties of high magnetocrystalline anisotropy, high coercivity and saturation magnetization, the nanotechnology is also applied to synthesis those ferrites.

Several methods for the synthesis of spinel ferrite particles including coprecipitation, sol-gel, hydrothermal synthesis, and mechanochemical techniques have been reported [3-5, 7]. Ultrasonic spray pyrolysis process has many advantages such as chemical homogeneity, multicomponent ceramics powder with homogeneous composition, available for mass production, no milling or calcination process requested for metals and ceramics, narrow particle size distribution and non-agglomeration. The main purpose of this work is to investigate the physical properties of the spherical NiZn ferrite particles at different annealing temperatures on magnetic behavior and microstructures.

2. Experimental Procedure

The precursor solution was prepared by dissolving a stoichiometric ratio of $Ni_{1-x}Zn_xFe_2O_4$ from mixture of $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_2 \cdot 9H_2O$ in distilled water at room temperature in molar ratio of 0.1 M

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and the atomization was carried out with an ultrasonic nebulizer generating aerosol droplets. Aerosol droplets were then inserted into a quartz tube reactor (inner diameter 50 mm, 1 m long) with an air stream as carrier gas at a flow rate of 1 *l*/min in a electric furnace at 1173 K. Evaporation from each droplet proceeded with no increase in temperature until each droplet consisted of precipitated salts with no remaining water. As the temperature increased, the nitrate salts melted but were retained in their individual spherical particle/droplet entities and decomposed in the mixed oxide powder spheres as the temperature increased. The fired spherical powders were collected by a bag filter and annealed at temperatures between 1273 K and 1673 K in air.

The crystalline phases were determined by XRD (X-ray Diffractometer) and the powder morphology was observed by FE-SEM (Field-Emission Scanning Electron Microscope). Magnetic characterizations were carried out with SQUID (Superconducting Quantum Interference Device) magnetometer and VSM (Vibrating Sample Magnetometer) at different temperatures.

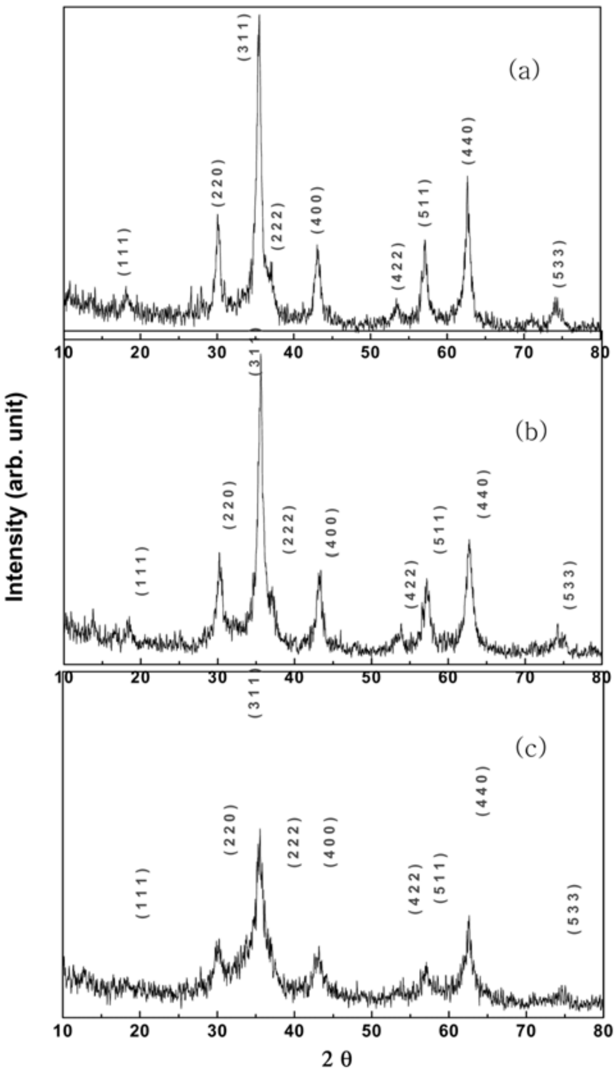


Fig. 1. XRD patterns of spherical NiZn ferrite powder synthesized by ultrasonic spray pyrolysis at different air blowing conditions(motor speed); (a) 350 rpm, (b) 600 rpm, and (c) 1000 rpm, respectively.

3. Results and Discussion

Nano-structured NiZn ferrite $Ni_{1-x}Zn_xFe_2O_4$ was single phase of spinel structure determined by XRD analysis as shown in Fig. 1. The electron micrographs of spherical NiZn ferrite particles were shown in Fig. 2, which presented an agglomerate-free NiZn ferrite particles by ultrasonic spray pyrolysis (USP) process in this study. The stoichiometric composition (x = 0.4, 0.6) of NiZn ferrite was selected to compare their properties

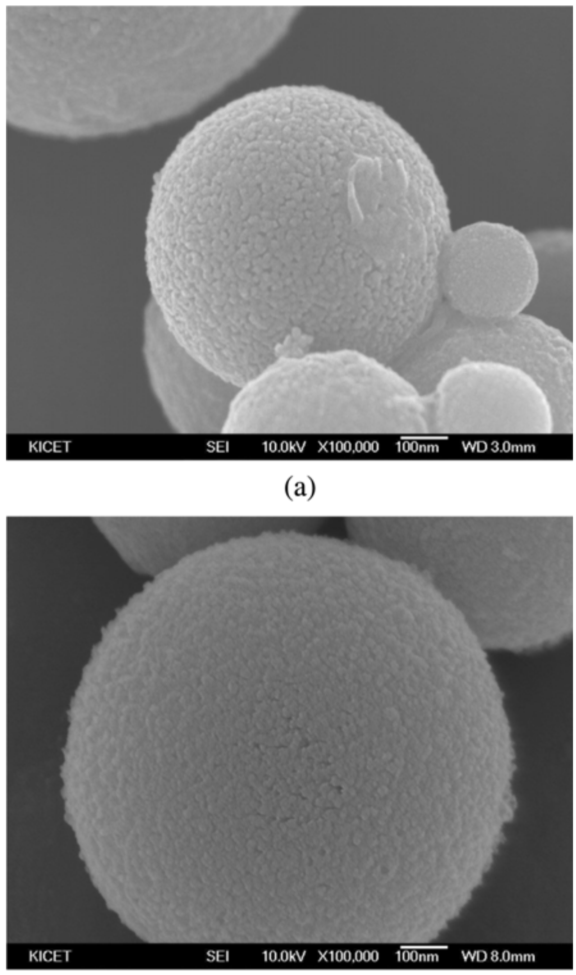


Fig. 2. FE-SEM images of spherical NiZn ferrite $Ni_{1-x}Zn_xFe_2O_4$ particles synthesized by ultrasonic spray pyrolysis process; (a) x = 0.4, (b) x = 0.6.

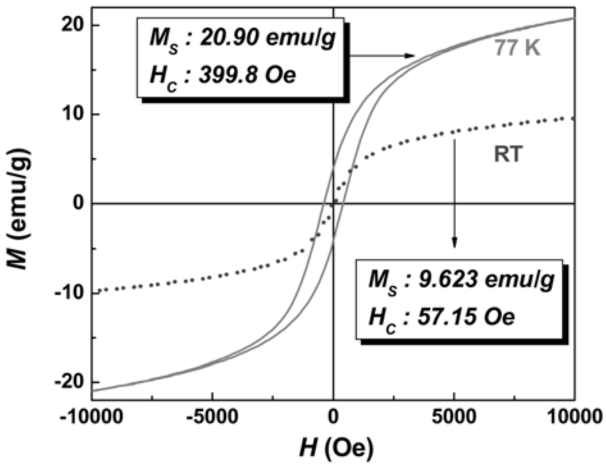


Fig. 3. Magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.4) powder measured at 77 K and room temperature.

with dependence of NiZn ferrite composition.

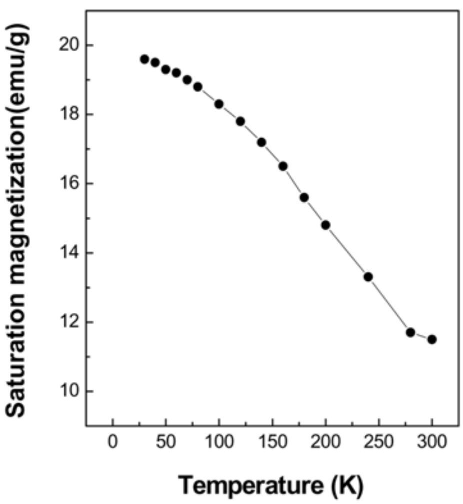
Normally, when the particle size of magnetic materials as ferrite becomes nano-sized the whole particle frame as nano-structured is strongly affected by thermal fluctuation even at elevating temperature from 77 K to room temperature 298 K due to the influence of thermal energy over the magnetic moment ordering originating the paramagnetic relaxation phenomena. As shown in Fig. 2, the nano-sized primary particles were formed in a bulk particle and expect to be a unit magnetic moment in applied field. Magnetic measurements of NiZn ferrite particles were also presented in Fig. 3. In order to describe the paramagnetic behavior of spherical NiZn ferrite particles, saturation magnetization (M_S) in the external field of 10 kOe and coercivity (H_C) was measured at 77 K to compare with the result at room temperature. It is revealed that the results of magnetic measurements were M_S = 9.6 emu/g, H_C = 57.1 Oe at room temperature and M_S = 20.9 emu/g, H_C = 399.8 Oe at 77 K, respectively, which indicate the differences in hysteresis loop of magnetic behavior.

In order to understand the magnetic behavior of nanostructural spherical NiZn ferrite particles, the temperature dependence of magnetization and coercivity in the range of 30~300 K can be considered to define the temperature- and relaxation time-dependent correlation. The temperature-dependent magnetization at a temperature under Curie point is generally followed by the Bloch's law [8, 9],

$$M(T) = M(0)(1 - BT^b) \text{ (for } T << T_C) \quad (1)$$

where B is Bloch constant and b is Bloch exponent. The values of B and b for samples can be obtained by fitting the measure data to Eq. (1).

The variation of saturation magnetization and coercivity as a function of temperature are shown in Fig. 4 for the nano-structured spherical NiZn ferrite particles. It is reported that the Bloch constant B values increase in reducing the particle size [9, 10]. As shown in Fig. 4, the dependence of the magnetization as a function of temperature seems to be saturated below about 25 K and above this temperature the thermal decrease of the magnetization is well described up to room temperature by the Eq. (1) of b = 3/2 [10], which is plotted showing a very clear relation up to room temperature with $B = 9.0 \times 10^{-5}\ K^{-3/2}$ as calculated in this study. Theories have shown that the fluctuation of surface moments is larger than those of the interior so that B of the surface atoms is about 2~3.5 times larger than that of the interior [9, 11]. This explains the large values of B in smaller particles,



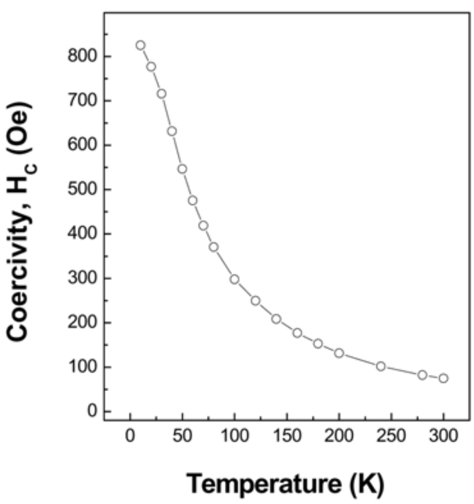


Fig. 4. Temperature-dependence of saturation magnetization and coercivity for $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.4) spherical particles with measuring temperature.

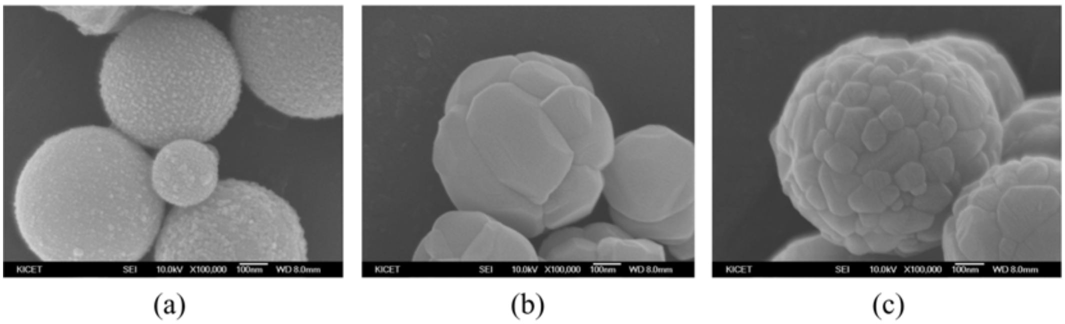


Fig. 5. FE-SEM images of $Ni_{1-x}Zn_xFe_2O_4$ nanostructured particles; (a) before annealing, (b) x = 0.4 and (c) x = 0.6 for annealed powder at 1273 K.

because the fraction of atoms on the surface is much higher in the case of smaller particles, compared to the bigger ones [12].

On the other hand, the spherical NiZn ferrite exhibited a strong dependence of coercivity on temperature. With decreasing temperature, the coercivity increased significantly below 100 K. Since the effective NiZn ferrite particle sizes were relatively small, its magnetic behavior of primary particles revealed from paramagnetic to ferromagnetic with decreasing temperature.

In order to identify the sintering behavior of spherical NiZn ferrite powder, the samples were annealed at 1273 K for 3 h in air. After annealing, the nano-structured NiZn ferrite particles were obtained with a typical morphology of primary particle like a polyhedral anisotropic growth as shown in Fig. 5. The variation of Ni/Zn composition ratio through cation diffusion mechanism in firing with Zn content(x) may be affected to the microstructure of the spherical NiZn ferrite particles after annealing and resulted in the different microstructure as shown in Fig. 5(b), (c). It is also revealed that the different microstructures of primary particle growth were affected by composition change of Zn content. Costa *et al*. [13] reported on sintering of NiZn ferrite nanopowders in variation of Zn content, which was studied on the dependence of Ni/Zn mole ratio and corresponded to the sintering property. It was also reported that the increases in Zn^{2+} concentration affected the sintering behavior as reducing the linear shrinkage at the point of maximum value and final density after sintering. As shown in Fig. 5, it was observed that the smaller size of primary particles after annealing was obtained from the relatively higher Zn content as a composition of x = 0.6.

The XRD patterns of those NiZn ferrite powders after annealing revealed good crystallinity of spinel structure but slighty disordered non-crystalline state was observed before annealing as shown in Fig. 6. The annealing effect of spherical NiZn ferrites powder can be explained from these XRD patterns, which is strongly related with atomic rearrangements in annealing process.

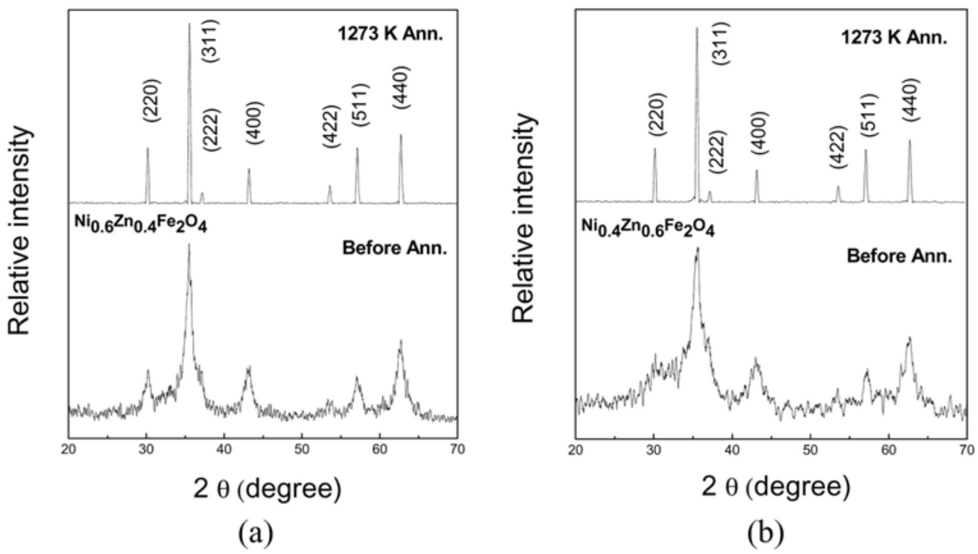


Fig. 6. XRD patterns of $Ni_{1-x}Zn_xFe_2O_4$ spherical powders; (a) x = 0.4, (b) x = 0.6.

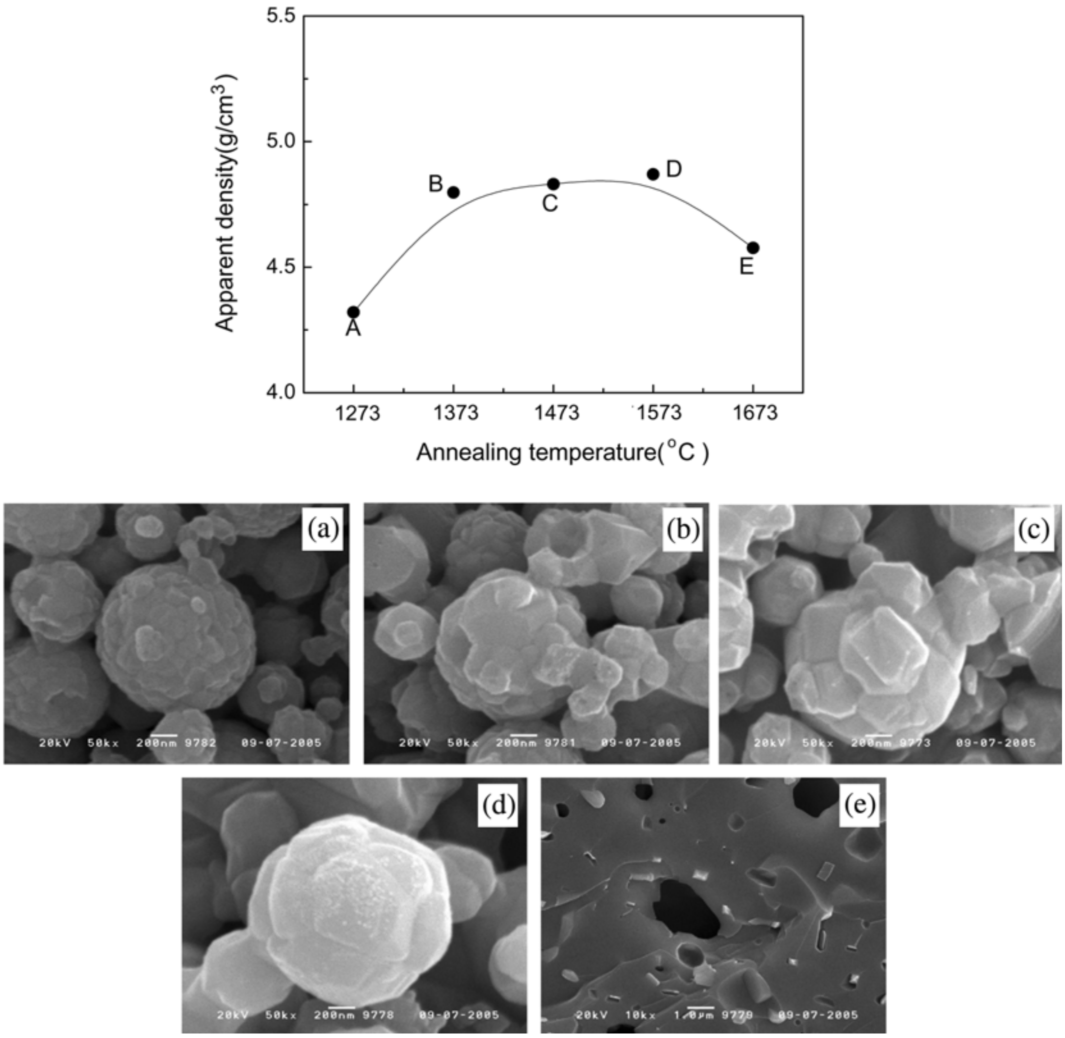


Fig. 7. Apparent density and SEM micrographs of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.4) powders annealed at each temperature;(a) 1273 K, (b) 1373 K, (c) 1473 K, (d) 1573 K, and (e) 1673 K, respectively.

In general, the mixed ferrites with the addition of the nonmagnetic Zn^{2+} ion increase the saturation magnetization which presents a dependence of stoichiometric composition for inverse-type spinel ferrites [14]. In other words, the substitution of magnetic ions in a ferromagnetic substance by non-magnetic ion can lead to an increase in the saturation magnetization and shows the maximum value between x = 0.4 and x = 0.6 in $Me_{1-x}Zn_xFe_2O_4$ (Me : Mg, Ni, Co, Mn). According to the previous work [15, 16], the Mössbauer measurements on $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.6) of high Zn concentration (x > 0.5) shows a paramagnetic behaviour at room temperature. It presents the typical magnetic behavior of nanosized spherical NiZn ferrite powder. Since the magnetic particles had an average size of about 10 nm as nanostructured, the doublet at room temperature could be attributed to the paramagnetic behavior of NiZn ferrite particles.

The apparent density measured by pycnometer for annealed NiZn ferrite powder was presented in Fig. 7. It is shown that densification between those separated spherical particles formed with each primary particles by annealing was proceeded up to 1573 K which reached a maximized value in this study. The intra-particle sintering after annealing was observed and showed rapid growth from those spherical particles with densification at temperature range of 1273~1573 K. It was also observed that significant grain coarsening was occurred with decreasing of apparent density at 1673 K.

In order to define the microstructures of formation and sintering of spherical NiZn ferrite powder, the schematic diagram was presented in Fig. 8. The Micro-droplet as starting formed a condensed particle seed of low salt concentration and finally become nano-sized primary particles because of such a low precursor concentration led to a decrease in the primary particle size. In the case of low salt concentration (Fig. 8a), the crystal-

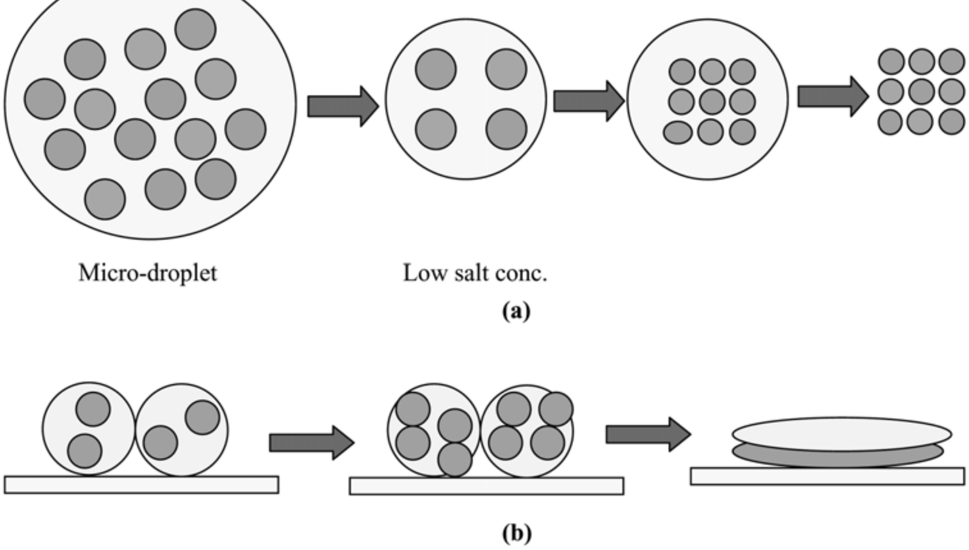


Fig. 8. Schematic diagram for variation of microstructure of spherical NiZn ferrite powder; (a) particle formation prepared by ultrasonic spray pyrolysis process, (b) annealing effect.

lites can easily come into contact with each other because insufficient molten salt is not available to hinder the crystallite growth. As a result, agglomerated primary particles with a smooth surface are formed and molten salt enhance crystallization with prevention of the formation of hard aggregates [17]. In annealing stage as shown in Fig. 8(b), the densification from inter-particle sintering occurred between those primary particles with rapid growth. As shown in Fig. 7(e) and Fig. 8(b), the spherical particle shape was disappeared and collapsed at 1673 K.

Fig. 9 shows the saturation magnetization measured between 77 K and 300 K of $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.4) powder annealed at temperatures between 1273 K and 1673 K to investigate the magnetic behavior of spherical NiZn ferrite powder. The magnetic characteristics of the annealed NiZn ferrite are not strongly affected as that of raw materials. Because the primary particle size was increased through the densification between the inter-particle sintering due to the multi-domain structure over grain growth, which is not proper to explain the paramagnetic relaxation phenomenon.

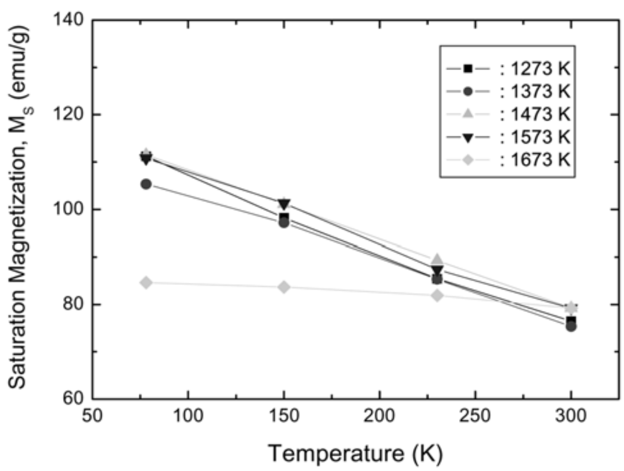


Fig. 9. Saturation magnetization of annealed $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.4) powders measured at different temperatures between 77 K and 300 K.

4. Conclusions

The spherical NiZn ferrite powders were successfully prepared from those metal nitrates aqueous solution by ultrasonic spray pyrolysis. Further annealing of as-prepared powder above 1173 K was needed to get enough magnetic properties. Abnormal particle growth was observed after annealing at 1273 K with Zn concentration, which showed a difference of morphology of primary particle growth. Nano-structured NiZn ferrite particles exhibited the paramagnetic behavior due to its nano-sized primary particle related to the magnetic disordering. Magnetic measurement revealed that NiZn ferrite particles showed relatively higher magnetization and coercivity at low temperature below 100 K due to its nanosized particles. The resulting morphology of spherical NiZn ferrite particle after annealing was affected by Zn concentration, Finally, the smaller grain size of primary particle at higher Zn concentration (x = 0.6 in $Ni_{1-x}Zn_xFe_2O_4$) was obtained in this study, which is related with cation diffusion mechanism. However, the saturation magnetization of NiZn ferrite powders annealed at 1273~1573 K had a small difference at each annealing temperature.

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