

Materials Science and Engineering B 111 (2004) 142-149



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Preparation of NiCuZn ferrite nanoparticles from chemical co-precipitation method and the magnetic properties after sintering

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Received 11 July 2003; accepted 5 April 2004

Abstract

NiCuZn ferrite nanoparticles with composition of Ni_xCu_yZn_{1-x-y}Fe₂O₄ (where x = 0.15-0.5 and y = 0-0.35) were prepared by the chemical co-precipitation method at various reaction temperatures with a final pH value of 12. From the analysis of X-ray diffraction patterns, the nanocrystalline NiCuZn ferrite particles could be obtained at pH = 12 and reaction temperature between 30 and 90 °C with the reaction time of 6 h. The particle size ranges from 2 to 60 nm by observation of transmission electron microscopy. Uniform size of cubic crystalline particles with particle size of about 30 nm were obtained at reaction temperature of 70 °C. The ferrite powders were compressed and sintered at various temperatures between 800 and 1000 °C for 2 h. According to experimental results, the NiCuZn ferrite powders with high Cu content could be sintered at about 800 °C. The density of the sintered Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ ferrite was 5.01 g/cm³ after sintering at 900 °C. The initial permeability μ of this sintered sample is about 390 at frequency of 1 MHz. Its H_c value is about 0.7 Oe and $B_s \cong 3100$ G. We found that Cu substitution for Ni in NiZn ferrite would enhance the densification of the ferrite and subsequently increases the μ value as well as B_s value, and decreases the H_c value of the sintered ferrite.

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Keywords: Chemical co-precipitation; Nanocrystalline NiCuZn ferrite; Magnetic properties

1. Introduction

NiZn ferrite have been used widely as high frequency ferrite because of their high electrical resistivity and high permeability in RF frequency region. Since the trend of technology development, the electronic device should be processed into microchip. The multilayer chip inductor (MLCI) [1–3] composes ferrite, inner conductor, and outer electrode. Silver is a suitable material for inner conductor, because of its characters of high conductivity, oxidative resistibility, and low cost. However the melting temperature of silver is 961 °C, which is too low to co-fire with NiZn ferrite at 1250 °C. Developing suitable process to fabricate smaller NiZn ferrite particles and modifying its composition to reduce the sintering temperature below 900 °C is necessary. From the viewpoint of thermal dynamics, the smaller particle own the higher surface free energy to achieve high density at low sintering temperature in shorter time.

Very fine ferrite particles can be produced by the chemical co-precipitation and sol-gel methods [4-8]. The size and shape of the ferrite particles are dependent on the synthesis process. It has been reported that the NiZn ferrite particles can be synthesized by chemical co-precipitation or hydrazine precursors method [6,9]. Actually, these methods demonstrated that high-density NiZn ferrite could be obtained at relatively low sintering temperature of about 1100 °C. However, this sintering temperature is still too high to co-fire with the Ag conductor. It had been shown that adding CuO to the NiZn ferrite could also lower its sintering temperature with conventional solid-state reaction method [10–13]. In this paper, we used the chemical co-precipitation method to fabricate the nano-size NiCuZn ferrite powders. Effects of reaction temperature on the particle size, shape, and crystallization of the precipitated particles are examined. The effects of Cu content on the powders' sintering behaviors,

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magnetic properties of the sintered ferrites, and microstructures are also investigated.

2. Experimental procedure

Nanocrystalline NiCuZn ferrite particles were synthesized by the chemical co-precipitation method. The starting materials are high-purity NiSO₄.6H₂O, CuSO₄.5H₂O, ZnSO₄·7H₂O, and FeSO₄·7H₂O. According to the formula of Ni_xCu_yZn_{1-x-y}Fe₂O₄ (where x = 0.15-0.5 and y = 0-0.35), each starting material was weighted, all added into 500 ml de-ionized water with concentration of 0.25 M, and stirring to complete dissolution. The NaOH solution is prepared by dissolving NaOH into 500 ml de-ionized water with concentration of 1 M. These two solutions mentioned above are mixed together by stirring, heated to the reaction temperature between 30 and 90 °C, and aerated uniformly by pumping air through porous glass to promote an oxidization reaction for 6 h. During oxidation, a small amount of NaOH solution was continuously added to keep the pH value at 12. After 6h of reaction, the precipitated particles are washed and filtered six times then dried at 60 °C. After drying, the co-precipitated ferrite particles were compressed into toroidal shape and sintered between 800 and 1000 °C for 2h.

The crystalline structure of the precipitated particles was examined by X-ray diffractometer (PW1830 generator, PHILIPS). The particle size and shape of the particles were characterized by transmission electron microscopy (TEM). The B–H loop of the sintered sample was measured with a B–H tracer (YOKOGAWA 3257), and their microstructure was observed with a scanning electron microscopy (SEM). The chemical compositions of the particles were analyzed by atomic absorption spectrometer (PERKIN ELMER 3100). The initial permeability (μ) and Quality factor (Q) were measured by HP4192A L.C.R meter at frequency of 1 MHz. The crystallization was characterized by a differential thermal analysis (Thermal Analyst 2000, Du Pont Instrument).

3. Results and discussion

The reaction temperature of the mixed solution and reaction time will influence the particle size, shape, and crystallization of the precipitated particles. Fig. 1 shows the X-ray diffraction patterns of the precipitated Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ particles which were reacted at various temperatures. We can see that the crystal structure of all the particles is the same as that of spinel NiZn ferrite. In Fig. 1(a), the broaden peaks of the X-ray diffraction pattern indicate that the particle size is very small and crystallization of NiCuZn ferrite is not good at the reaction temperature of 30 °C. The X-ray peaks of Fig. 1(b) are sharper than that of Fig. 1(a), this means that the particles



Fig. 1. X-ray diffraction patterns of the Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ particles precipitated at: (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C. The pH value is 12 and the reaction time is 6 h.

precipitated at 50 °C are larger and better crystallization than that of 30 °C. The more sharp peaks in Fig. 1(c) and (d) show better crystallization and larger grain size at higher reaction temperature of 70 and 90 °C from the calculation of Scherrer's formula [14].

Fig. 2(a–d) shows the TEM images of the particles which precipitated at the reaction temperature of 30, 50, 70, and 90 °C, respectively. The particles are very small and agglomerated together like colloidal at the reaction temperature of 30 °C as shown in Fig. 2(a). The average particle size is only about 2 nm. As the reaction temperature increases to 50 °C, the average particle size grows to about 15 nm and the particle shape is granular as shown in Fig. 2(b). The shape of particles is cubic and the particle size becomes very uniform at the reaction temperature of 70 °C, as shown in Fig. 2(c). The particle size is about 30 nm. As the reaction temperature increases to 90 °C, the shape of precipitated particles becomes irregular and the distribution of particle size is about 60 nm.



(a) 30°C



100nm



Fig. 2. Transmission electron micrographs of $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$ particles precipitated at: (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C. The pH value is 12 and the reaction time is 6 h.

The solid lines of Fig. 3 show the composition analysis of the precipitated particles at various reaction temperatures by AA. The dash lines are the estimated contents of various oxides from the weighted starting materials. The deviations of NiO, CuO, ZnO, and Fe₂O₃ contents in precipitated particles from estimated values are small and acceptable at the reaction temperatures between 30 and 90 °C.

All of the sintering samples were fabricated from the precipitated particles which is obtained at the reaction temperature of 70 °C and pH = 12. Fig. 4 shows the dependence of the sintering density on the sintering temperature of the precipitated particles with different Cu content. It is obvious that the Cu substitution for Ni in NiZn ferrite will enhance the sintering density of the particles. This is owing to the Cu oxide has a lower melting point than that of the other oxides. The melting points of Fe₂O₃, NiO, CuO, and ZnO are 1565, 1984, 1320, and 1975 °C, respectively. The sintered density in Fig. 4 reveals that the Cu substitution for Ni in NiZn ferrite enhances the densification largely as the sintering temperature is lower than 950 °C. When the sintering temperature is 850 °C, the ferrites' density is increased from 3.05 to 4.82 g/cm³ as Cu mole ratio increases from 0 to 0.11 and 0.31. At this Cu content range (Cu mole ratio = 0.11–0.31), the Cu content does not obviously affect the sintering density as the sintering temperature is higher than 850 °C. The sintering density of the Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ particles is



Fig. 3. Relationships among estimated composition, AA composition analysis of precipitated particles and reaction temperature. The pH value is 12 and the reaction time is 6 h.

about 5.01 g/cm³ at 900 $^{\circ}$ C; this is 93.2% of the theoretical density.

The SEM micrographs in Fig. 5 indicate that the fracture surfaces of the ferrites sintered at 800 °C. Fig. 5(a) shows the pure NiZn ferrite, which contains no Cu ion, reveals no sintering performance and only compact particles. Fig. 5(b) shows the particles with composition of Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ reveals only a little sintering phenomenon. Fig. 5(c) displays the powder with composition of Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ has slight sintering performance at 800 °C, but not very dense. Its grain size is about 1 μ m.



Fig. 4. The relationship between sintering density and sintering temperature of precipitated particles with various Cu content.



(a) $Ni_{0.49}Zn_{0.51}Fe_2O_4$



(b) $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$



(c) $Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe_2O_4$

Fig. 5. Scanning electron micrographs of the fracture surface of: (a) $Ni_{0.49}Zn_{0.51}Fe_2O_4$, (b) $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$, and (c) $Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe_2O_4$ sintered at 800 $^\circ C$ for 2 h.



(a) $Ni_{0.49}Zn_{0.51}Fe_2O_4$



(b) $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$



(c) $Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe_2O_4$

Fig. 6. Scanning electron micrographs of the fracture surface of: (a) $Ni_{0.49}Zn_{0.51}Fe_2O_4$, (b) $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$, and (c) $Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe_2O_4$ sintered at 900 $^\circ C$ for 2 h.



(a) $Ni_{0.49}Zn_{0.51}Fe_2O_4$



(b) $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$



(c) $Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe_2O_4$

Fig. 7. Scanning electron micrographs of the fracture surface of: (a) $Ni_{0.49}Zn_{0.51}Fe_2O_4$, (b) $Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe_2O_4$, and (c) $Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe_2O_4$ sintered at 1000 °C for 2 h.



Fig. 8. DTA analysis of the Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ powders.

Fig. 6(a) shows the pure NiZn ferrite, which contains no Cu ion, reveals no sintering performance at 900 °C yet. Fig. 6(b) and (c) show the powder with compositions of Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ and Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄, respectively, obviously they all reveal sintering phenomenon at 900 °C. Their grain sizes are almost the same and range from 2 to 5 μ m.

Fig. 7(a) shows the pure NiZn ferrite, which contains no Cu ion, reveals slight sintering performance at 1000 °C, but not dense. The grain size is about 0.7 μ m. Fig. 7(b) shows the powder with composition of Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄, reveals sintering performance at 1000 °C obviously. Its grain size ranges from 6 to 10 μ m. On the other hand, the powder with composition of Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ reveals the phenomenon of liquid-phase sintering on grain boundary at 1000 °C, as shown in Fig. 7(c). Fig. 8 shows the differential thermal analysis (DTA) of the Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄

powder, there is an endothermic peak near $1052 \,^{\circ}C$ with the heating rate of $5 \,^{\circ}C/\text{min}$. From the analysis of element line scanning by SEM, we confirm that the phase segregated on grain boundary of Fig. 7(c) is Cu-rich phase.

Comparing the scanning electron micrographs of Figs. 5–7, it can be seen that the grain size is increased significantly with increasing the sintering temperature. At the sintering temperature of 900 °C, substantial grain growth occurs in which the ferrites' grain is cubic like and well crystalline if it contains Cu ion. As the sintering temperature increases to 1000 °C, some grain growth occurs in the pure NiZn ferrite. But the grain becomes quite large and round shape if the ferrite contains Cu ion. A second phase can be clearly observed at the ferrite's grain boundary as the content of the mole ratio of Cu increases to 0.31.

The density and grain size of the ferrite increase with increasing sintering temperature, and they would affect magnetic properties directly. Generally, the magnetization mechanism of soft magnetic materials like NiZn ferrite is domain wall motion, which generates high initial permeability (μ). Although pores and grain boundary would obstruct the movement of domain wall, the fewer amounts of pores and grain boundary could be obtained at higher sintering temperature and leads easy movement of domain wall and high initial permeability. The magnetic properties of all ferrites were measured at 1 MHz. Fig. 9 shows the variation of initial permeability (μ) with sintering temperature (T_s) of various ferrites. The μ value of all ferrites is below 70 at 800 °C, this is due to the incompletely sintering (see Fig. 5). The μ value of the ferrite which contains Cu ion increases rapidly with increasing sintering temperature as $T_{\rm s}$ < 900 °C. The μ value of the Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ ferrite increases from 25 to 340 as T_s increases from 800 to 900 °C and it gradually saturated at higher temperature.



Fig. 9. Variation of the initial permeability with sintering temperature of various ferrites.





Fig. 10. Variation of the Q value with sintering temperature of various ferrites.

The μ value of the Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ ferrite reaches their maximum value ($\mu \cong 415$) at $T_s \cong 950$ °C, and then decreases slowly at higher temperature due to the movement of domain wall was obstructed by Cu-rich phase which is segregated at the grain boundary [see Fig. 7(c)]. The ferrite containing no Cu ion has a lower μ value because they are difficult to dense during sintering, as shown in the solid circle line of Fig. 9.

Fig. 10 shows the variation of the Quality factor (*Q*) with sintering temperature of various ferrites. The maximum *Q* value of the Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ ferrite is about 90 which occurs at $T_s \cong 850$ °C, this T_s is about 50 °C lower than the T_s of maximum μ value (see Fig. 9). The *Q* value depends on the ferrites' microstructure, e.g. pores, grain size, and second phase etc., and all will influence its *Q* value. The *Q* value of the pure NiZn ferrite is markedly lower as $T_s < 900$ °C because of incomplete densification of the sample. The maximum *Q* value of the pure NiZn ferrite is occurred at much higher sintering temperature.

As T_s increases from 800 to 1000 °C, the H_c values of the ferrites are all decreased with increasing T_s , as shown in Fig. 11. But, all of the B_s values increase with increasing T_s , as shown in Fig. 12. Higher sintering temperature and higher Cu content imply a larger grain size and better crystalline in the ferrite, thereby allowing for easier domain movement, which leads lower H_c value and high B_s value. Consequently, the Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ and Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ ferrites produce a lower H_c value (below 1.5 Oe) and higher B_s value (more than 3000 G) as T_s is higher than 900 °C. The pure NiZn ferrite without Cu or sintering temperature below 900 °C, they would incompletely dense and contain non-magnetic pores, produced high H_c and low B_s . Comparing two fer-

Fig. 11. The relationship between H_c value and sintering temperature of various ferrites.

rites Ni_{0.39}Cu_{0.11}Zn_{0.5}Fe₂O₄ and Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ in Figs. 9–12, reveals that a higher Cu (lower Ni) content yields a higher μ value, as well as a lower Q value, H_c value, and B_s value because the spin moment of Cu²⁺ ion is 1 μ_B and Ni²⁺ is 2 μ_B . If high μ value and low H_c value are expected, high Cu content in the ferrite is preferred. On the other hand, if high B_s value and Q value are expected, less Cu content but enough densification of the ferrite is favored.



Fig. 12. The relationship between B_s value and sintering temperature of various ferrites.

4. Conclusions

We have preparing the NiCuZn ferrite nanoparticles from the chemical co-precipitation method. Uniform size of cubic crystalline particles with particle size of about 30 nm were obtained at reaction temperature of 70 $^{\circ}$ C and pH = 12. The ferrite powders with high Cu content could be sintered at about 800 °C. The Cu content in the ferrite is an important factor for not only enhancing the densification of the ferrite but also improving the ferrites' magnetic properties. The optimal Cu content depends on which magnetic property expected. The ferrite with higher Cu content could be sintered at lower temperature. Powder with the composition of Ni_{0.18}Cu_{0.31}Zn_{0.51}Fe₂O₄ after sintering at 850 °C, the density is 4.82 g/cm^3 , the initial permeability is about 200 at frequency of 1 MHz and the H_c is about 2 Oe. When the sintering temperature increased to 900 °C, the density is about 5.01 g/cm³, the initial permeability is about 390; the $H_{\rm c}$ would decrease to 0.7 Oe and $B_{\rm s}$ is about 3000 G. The Cu substitution for Ni in NiZn ferrite would enhance the densification of the ferrite and subsequently increases the μ value, B_s value, and decreases the H_c value of the sintered ferrite.

Acknowledgements

This work was supported by the National Science Council and Ministry of Economic Affairs of Taiwan through Grant

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