

# Low-Temperature Sintering of (Ni,Zn)Fe<sub>2</sub>O<sub>4</sub> by Hot Isostatic Press

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## Abstract

Ni-Zn ferrite powder having average particle size of 20-30 nm was prepared from an aqueous solution, and was then sintered at a relatively low temperature of 800°C for 1 h, applying 200 MPa of isostatic pressure; hot isostatic press (HIP). Relative density of sintered Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub> was 95%, whereas that obtained under atmospheric pressure was 53%. High density enough to fabricate electric devices was obtained without any additive; e.g. CuO, by the HIP treatment of the active powder. Furthermore, higher density 98% was obtained for Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub>. This process will be applicable to fabricate multilayer chip inductors, in which Ni-Zn ferrite needs to sinter with silver electrode at below the melting point (960°C). The magnetic properties of Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub> with 98% in relative density were measured as follows; maximum flux density at 10 Oe (B<sub>10</sub>)=1366 Gauss, coercive force (H<sub>c</sub>)=2.8 Oe, and remanent flux density (Br)=506 Gauss.

Key Words: hot isostatic press, low temperature, sintering, Ni-Zn ferrite, aqueous solution

## 1. INTRODUCTION

Ni-Zn ferrite ((Ni,Zn)Fe<sub>2</sub>O<sub>4</sub>) has a relatively high electric resistivity and a low power loss even at high frequency. Ni-Zn ferrite is a candidate for the material for multilayer chip inductor. In order to obtain high Q, silver is used as internal electrode. However, high temperature of 1200-1350°C is generally needed to sinter the Ni-Zn ferrite. These temperatures are higher than the melting point of silver; 960°C. Hence, Ni-Zn-Cu ferrite, of which sintering temperature is lower than the melting point of silver, is used to fabricate the chip inductor [1]. However, the saturation magnetization of Ni-Zn ferrite is decreased by the addition of CuO [2]. In this study, the Ni-Zn ferrite powder with ultra fine particle size was prepared from aqueous solution [3], and was then sintered at 800°C by the use of hot isostatic press (HIP).

## 2. EXPERIMENTAL

### 2.1 Preparation of Ni-Zn ferrite from aqueous solution

NiSO<sub>4</sub>·6H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, FeSO<sub>4</sub>·7H<sub>2</sub>O and NaOH (Wako Pure Chem. Ind. Ltd.) were used as starting materials. Figure 1 shows the apparatus for the preparation of (Ni,Zn)Fe<sub>2</sub>O<sub>4</sub> powders. Aqueous solution of sulfates with the composition corresponding to Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub> or Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub> (Ni<sup>2+</sup>+Zn<sup>2+</sup>+Fe<sup>2+</sup> <0.1 mol/l) was charged into the flask. NaOH solution was added to the sulfate solution to precipitate the mixed hydroxide. This hydroxide was then oxidized at 70-75°C for 2 h, bubbling an air to prepare the Ni-Zn ferrite. The precipitate was separated by centrifugation and was washed by water and ethanol. After drying at 60°C for 12 h, the cake was crushed and ground to make a Ni-Zn ferrite powder. The powders were characterized by X-ray diffraction (XRD), induction coupled plasma (ICP) analysis and scanning electron microscope (SEM).

Ni-Zn ferrite powders were also prepared by conventional process. NiO, ZnO and Fe<sub>2</sub>O<sub>3</sub> powders (Wako Pure Chem. Ind. Ltd) were mixed in a zirconia pot mill with zirconia balls. The mixed powder was dried at 60°C for 12 h, and was calcined at 800°C for 3 h. The calcined powder was ground in a mortar.

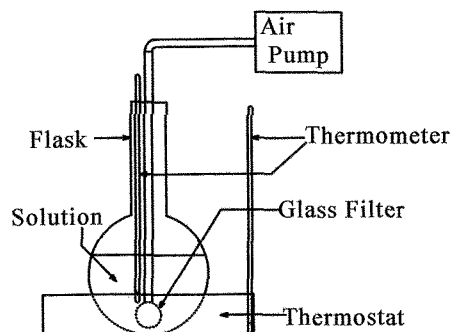


Fig. 1. Apparatus for the preparation of ferrite from aqueous solution.

### 2.2 HIP sintering of Ni-Zn ferrite

Ni-Zn ferrite powder (1.5-3.0 g) was pressed into a cylindrical compact by CIP (cold isostatic press, 200 MPa, 10 min). The compact was heated at 400°C for 0.5-1 h in vacuum to remove the adsorbed water. Aluminum or Pyrex glass capsule containing a compact was evacuated at 400°C, and was then sealed. The compact was embedded in ZrO<sub>2</sub> powder to prevent the reaction with capsule. The capsule was heated at 800°C for 1 h under a HIP pressure of 50-200 MPa to sinter the compact. The density of sintered Ni-Zn ferrite was measured by Archimedes' method. The Ni-Zn ferrite after HIP treatment was characterized by XRD. The fracture surface was observed by SEM.

2.3 Characterization

Original powder of Ni-Zn ferrite was charged into a sample vessel (7 mm inner dia. and 12 mm height), and the sintered Ni-Zn ferrite was shaped as a troidal form (10 mm in outer dia., 2.5 mm in inner dia. and 2 mm thick). The sample vessel and the troidal were measured by B-H curve tracer (Riken Denshi Co., Ltd), respectively, to determine the magnetic properties.

3. RESULTS AND DISCUSSION

3.1 Preparation of Ni-Zn ferrite powders

Figure 2 shows the XRD patterns of the powder obtained from aqueous solution. The powder was identified as Ni-Zn ferrite. In addition, the composition of the powder, which was determined by ICP analysis, was the same as that of starting mixture.

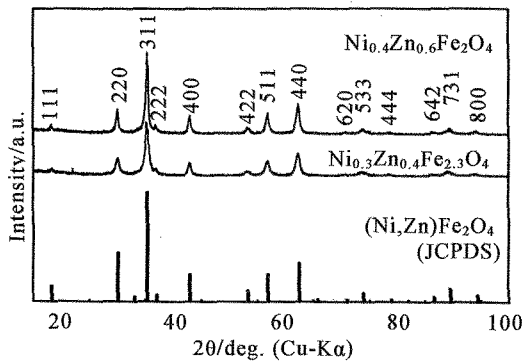
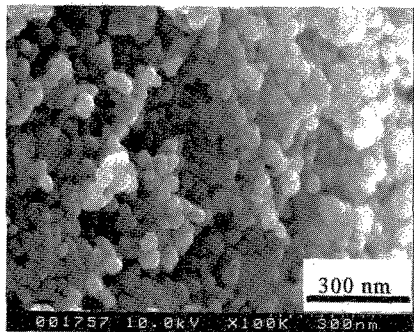
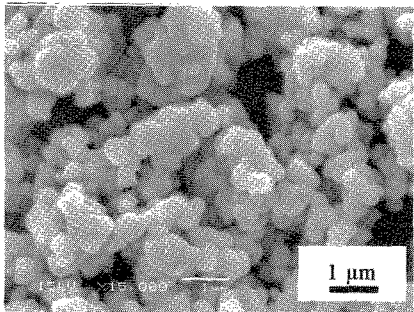


Fig. 2. X-ray diffraction patterns of the powder prepared from aqueous solution.



(a) Powder prepared from aqueous solution



(b) Powder prepared by conventional heating process.

Fig. 3. Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub> powders (SEM).

Figure 3 shows SEM photographs of the Ni-Zn ferrite powders. Particle size and size distribution were measured from these photographs. The particle size of the Ni-Zn ferrite prepared by aqueous solution was 20-30 nm with narrow particle size distribution. This was comparable to those obtained from Scherrer's equation; 16 nm for Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub> and 22 nm for Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub>. On the other hand, particle size obtained by conventional process was 0.3-2.0 μm with a wide size distribution.

The saturation magnetization of the powders obtained from solution was 30 emu/g for Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub> and 50 emu/g for Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub>. On the other hand, the saturation magnetization of the powder (Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub>) prepared by the conventional process was 62 emu/g.

3.2 HIP sintering of Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub>

Figure 4 shows the relative density of sintered Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub>. At 600°C, the relative density obtained for the powder from aqueous solution was 78%, applying an isostatic pressure of 200 MPa. On the other hand, the relative density for the powder obtained by conventional process was 66%.

The HIP temperature was raised to 800°C to obtain a high density. High density of 95% was obtained under 200 MPa for the powder from aqueous solution, whereas the density for the conventional powder was 90%. These results suggest that the fine particles size (20-30 nm) and narrow size distribution contribute to the densification. Under the atmospheric pressure, the temperature 800°C was insufficient to densify Ni-Zn ferrite. It was concluded that the high density was achieved at low temperature without any additive by HIP sintering of the Ni-Zn ferrite powder prepared from aqueous solution.

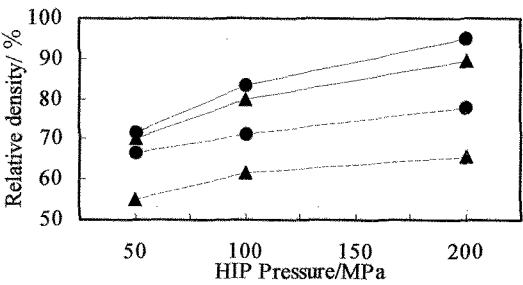


Fig. 4. Relative density of Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub>.  
(●):Powders prepared from aqueous solution  
(▲):Powders prepared by conventional heating process)  
(—):Sintered at 800°C  
(---): Sintered at 600°C)

3.3 HIP sintering of Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub>

According to Harvey et al., permeability of Ni-Zn ferrite reveals the maximum in the composition of Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub> [4]. Hence, Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub> was prepared from the solution and was then sintered by HIP.

Figure 5 shows the relative density of sintered Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub>. High densities were obtained compared to those of Ni<sub>0.4</sub>Zn<sub>0.6</sub>Fe<sub>2.0</sub>O<sub>4</sub>. The maximum

density obtained at 800°C under 200 MPa was 98%. Sintering temperature of  $\text{NiFe}_2\text{O}_4$  is generally higher than that of  $\text{ZnFe}_2\text{O}_4$ .  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$  containing a small amount of Ni appears to be easy to sinter.

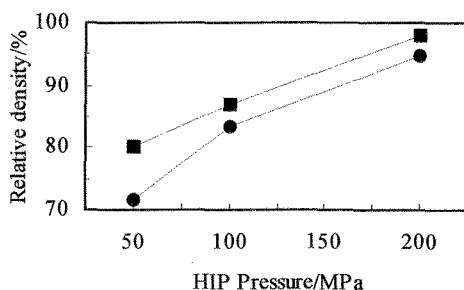
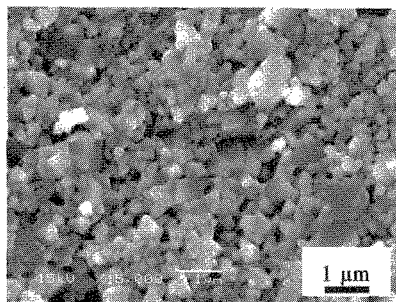


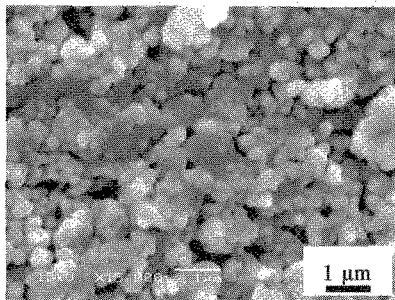
Fig. 5. Relative density of  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$ . (■:  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$ , ●:  $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.0}\text{O}_4$ ) (Sintering temperature: 800°C)

### 3.4 Characterization

Figure 6 shows the microstructure of the sintered Ni-Zn ferrite. Grain size of Ni-Zn ferrite prepared from aqueous solution was increased by HIP, because particle size of original powder was 20-30 nm. This is due to the fine particle size of ferrite obtained from aqueous solution. On the other hand, grain growth was not observed in the microstructure obtained from the powder prepared by conventional process.



(a) Powder used for sintering ;  
From aqueous solution.



(b) Powder used for sintering ;  
Conventional heating process.

Fig. 6. Microstructures of  $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.0}\text{O}_4$  sintered by HIP (SEM). (HIP pressure : 200 MPa)

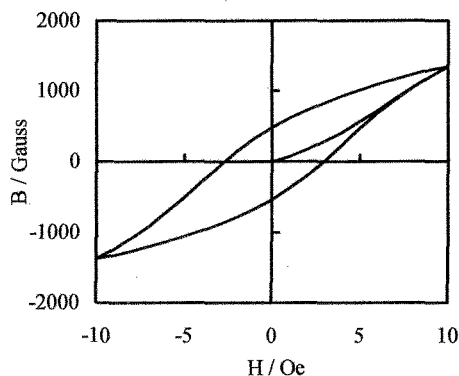


Fig. 7. B-H curve for  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$  obtained by HIP sintering.

Figure 7 shows the B-H curve for sintered  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$  with 98% in relative density. However, maximum flux density at 10 Oe ( $B_{10}$ ) and remanent flux density ( $B_r$ ) were relatively low, and coercive force ( $H_c$ ) was large;  $B_{10}=1366$  Gauss,  $H_c=2.8$  Oe,  $B_r=506$  Gauss.

Some reasons are considered to understand the degradation of magnetic properties. When the Ni-Zn ferrite powders prepared from aqueous solutions were heated at 800°C for 1h, the weight decreased; 9 mass% for  $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.0}\text{O}_4$  and 7 mass% for  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$ . These weight losses are due to the evolution of adsorbed water [5], leading the decrease of density in capsule HIP. On the other hand, Shimoiizaka et al. deduced that Ni-Zn ferrite powder prepared from aqueous solution contains random distribution of cations [6]. In addition, the residual stress in the Ni-Zn ferrite after HIP appears to degrade the magnetic properties. In the polycrystalline Ni-Zn ferrite, coercive force is inversely proportional to the grain size [7]. As shown in Fig. 6, the grain size after HIP was relatively small as 0.2-0.5  $\mu\text{m}$ . From these reasons, the magnetic properties of HIP treated Ni-Zn ferrite are still not enough for the commercial use.

In order to improve the magnetic properties, the study will be continued from the viewpoints of the removal of adsorbed material, the control of microstructure and the removal of residual stress.

### 4. SUMMARY

Ni-Zn ferrite powders prepared from aqueous solution were sintered at low temperature, using HIP technique.  $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.0}\text{O}_4$  and  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$  powders were prepared by oxidizing the emulsion of hydroxides containing Ni, Zn and Fe. Fine powders with 20-30 nm in particle size were obtained. The relative densities of  $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_{2.0}\text{O}_4$  and  $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$  obtained at 800°C under 200 MPa were 95% and 98%, respectively. Grain size of Ni-Zn ferrite prepared from aqueous solution was increased by HIP, whereas grain growth was not observed for the powder prepared from

conventional process. The magnetic properties of Ni<sub>0.3</sub>Zn<sub>0.4</sub>Fe<sub>2.3</sub>O<sub>4</sub> with 98% in relative density were B<sub>10</sub>=1366 Gauss, H<sub>C</sub>=2.8 Oe, and Br=506 Gauss. It is concluded that high density was achieved at low temperature without any additive using HIP technique and Ni-Zn ferrite powder prepared from aqueous solution.

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