

# Fine Iron Oxide Powder as a Raw Material of Soft Ferrites<sup>†</sup>

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## Abstract:

JFE Steel Group developed a new fine iron oxide powder "JC-FH04." Fine magnetic powders, which are obtained by applying a wet synthesis method, are oxidized by heating to produce high purity fine iron oxides with specific surface areas above  $1.2 \times 10^4$  m<sup>2</sup>/kg. It is confirmed that the sintering temperature of NiCuZn ferrites made from the developed fine iron oxide is lower than that made from a conventional spray roasted iron oxide.

## 1. Introduction

Recently, electric components have been becoming smaller and thinner size with the recent progress of technology to downsize portable electronic equipment. The multilayer chip inductors are widely used in such electronic equipment for signal transmission. They are manufactured by laminating the magnetic material layers such as NiCuZn ferrites, and electrode layer, which makes a coil, such as Ag, and then by co-firing them integrally at a low temperature of about 900°C which is below the melting point of the electrode layer<sup>1</sup>). Therefore, ferrite powder, which is prepared from iron oxide, is ball-milled for many hours to obtain fine milled powders which reduce the sintering temperature at 900°C or below. The thickness of each ferrite layer is decreasing with downsizing or performance improvement of multilayer chip inductors.

To decrease the thickness of the ferrite layer and to obtain finer ferrite particles in a short ball-milling time, iron oxide (hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), which is the main raw material of ferrite accounting for about 70% of it

by weight, has been demanded to have smaller particle aggregations.

The iron oxide used for soft ferrite is generally manufactured by purifying waste pickling acid (ferrous chloride solution) generated from the ironmaking plant, and then by spray-roasting the purified ferrous chloride solution. JFE Steel Group also manufactures iron oxide by using a similar method<sup>2</sup>). The spray-roasting, however, produces iron oxide powder with a specific surface area only in an approximate range from  $3 \times 10^3$  to  $5 \times 10^3$  m<sup>2</sup>/kg (particle size from 0.2 to 0.4  $\mu$ m). Thus it is difficult to manufacture fine iron oxide powder having a specific surface area above  $1 \times 10^4$  m<sup>2</sup>/kg (particle size smaller than 0.1  $\mu$ m) by spray-roasting<sup>3</sup>).

Regarding the formation of fine iron oxide powder for ferrite, some papers reported about the wet formation process using ferric chloride solution or ferrous sulfate solution as the raw material<sup>4,5</sup>). The method using ferric chloride solution, however, has problems of high raw material cost and long reaction time (48 to 72 h)<sup>4</sup>). The iron oxide manufactured by the method also contains Cl about 500 ppm by mass<sup>4</sup>). On the other hand, the iron oxide manufactured from ferrous sulfate solution contains SO<sub>4</sub> about 0.3 mass%<sup>5</sup>). The iron oxide usually contains some amount of the impurities coming from the starting raw materials, such as Cl or SO<sub>4</sub>.

In this paper, the manufacturing conditions of fine iron oxide powder with only a small amount of Cl coming from the starting raw materials, were investigated, by using the ferrous chloride solution generated from ironmaking plant. In addition, the effect of the particle size of iron oxide on the sintering behavior and magnetic properties of NiCuZn ferrites were also investigated.

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## 2. Experimental Procedure

### 2.1 Preparation of Fine Iron Oxide Powder

The selected starting materials for fine iron oxide powder were ferrous chloride solution for high purity iron oxide, prepared by purifying waste hydrochloric acid generated from the pickling of steel sheet<sup>2)</sup>, and industrial grade high purity ferric chloride solution and sodium hydroxide solution.

The ferrous and the ferric chloride solution were mixed together (hereafter, mixed iron chloride solution), with the ratio of ferrous to ferric chloride ranging from 10:0 to 7:3 ( $\text{Fe}^{3+}/(\text{total Fe}) = 0$  to 30 mol%). The Fe concentration of the mixed iron chloride solution ranged from 0.75 to 3.6 kmol/m<sup>3</sup>, and the concentration of the NaOH solution ranged from 1.2 to 3.5 kmol/m<sup>3</sup>.

The mixed iron chloride solution was neutralized by the NaOH solution and the Fe concentration was controlled to be 0.5 kmol/m<sup>3</sup>. After neutralizing, the solution was oxidized by air under an alkaline condition at 80°C, to synthesize the magnetite fine particles. The byproduct NaCl was desalted by washing the product with pure water, and the magnetite fine particles were dried and pulverized. The magnetite powder was further heated in air to oxidize at a temperature between 480°C and 500°C to obtain the hematite powder.

The obtained iron oxide powder was identified by an X-ray diffractometer (RINT-1500, Rigaku Corp.). The specific area was measured by the BET method (4-SORB U2, Yuasa-Ionics Co., Ltd.). The particle size distribution was measured by a laser-diffraction particle size distribution analyzer (Microtrac X100, Nikkiso Co., Ltd.). The particle shapes of powder was observed by SEM (S-4100, Hitachi, Ltd.). The contents of Cl and SO<sub>4</sub> in the iron oxide were analyzed by a fluorescent X-ray analyzer (Simultics 12, Rigaku Corp.). The amount of Na was analyzed by an atomic absorption spectrometer (Z-6100, Hitachi, Ltd.). The amount of SiO<sub>2</sub> was analyzed by a plasma emission spectrometric analyzer (ICPS-7500, Shimadzu Corp.).

### 2.2 Fabrication and Properties Evaluation of Ferrite Core Using Fine Iron Oxide Powder

Fine iron oxide having a specific surface area of  $1.29 \times 10^4$  m<sup>2</sup>/kg and 770 ppm of Cl, and conventional spray roasted iron oxide JC-CPW (manufactured by JFE Chemical) prepared by the spray-roasting method, having a specific surface area of  $4.9 \times 10^3$  m<sup>2</sup>/kg and 770 ppm of Cl were used as the raw materials for ferrites. NiO, CuO, and ZnO of a general industrial grade were also used. Each of the raw materials was

weighed in the composition of Ni<sub>0.18</sub>Cu<sub>0.24</sub>Zn<sub>0.6</sub>Fe<sub>1.96</sub>O<sub>4</sub>, and then they were ball-milled with distilled water for 16 h. The mixtures were calcined at 750°C for 2 h. The calcined powders were ball-milled for 2 h, then 0.5% of polyvinyl alcohol was added to the milled powder. The size and shape of individual powder particles were observed by SEM.

The mixed powders with 0.5% of polyvinyl alcohol were pressed into toroidal shape (19 mm in outer diameter, 10 mm in inner diameter, and 4.5 mm in height) under a pressure of 120 MPa. The green bodies were sintered in air at a temperature between 850°C and 950°C for 3 h.

The sintered density of the toroidal core was calculated from the dimensions and weight of the core. The initial permeability of the core,  $\mu_i/\mu_0$  ( $\mu_0$  is the permeability in vacuum), was measured by an LCR meter (4285A, Hewlett-Packard Development Company, L.P.).

## 3. Results and Discussion

### 3.1 Investigation of Wet Process for Manufacturing Fine Iron Oxide Powder

Figure 1 shows the specific surface area of magnetite obtained by varying the content of ferric chloride in the mixed iron chloride solution,  $\text{Fe}^{3+}/(\text{total Fe})$ , in a range from 0 to 30 mol%. A larger content of ferric chloride,  $\text{Fe}^{3+}/(\text{total Fe})$ , increased the specific surface area of the formed magnetite.

Regarding the formation of magnetite by the wet process, coprecipitation method<sup>6)</sup> and air oxidation method<sup>7,8)</sup> have been reported. These reactions of magnetite formation are expressed by the following equations:

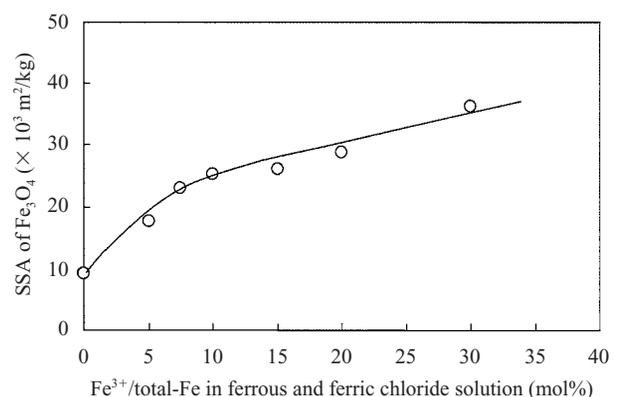
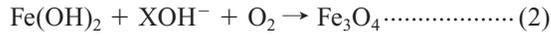


Fig. 1 Effect of Fe<sup>3+</sup> concentration in ferrous and ferric chloride solution on specific surface area (SSA) of Fe<sub>3</sub>O<sub>4</sub> particles



Equation (1) is the reaction of the coprecipitation method to form magnetite. In the reaction, it is known that fine magnetite particles are formed in an alkali solution<sup>6</sup>. Equation (2) is the reaction of the air-oxidation method to form magnetite. The particle sizes formed in this reaction are larger than those of the coprecipitation method, being of submicron order<sup>7,8</sup>. Some reports indicate that the particle shape depends on the kind of anion in the applied raw material solution, the equivalent ratio to alkali ( $2\text{OH}^-/\text{Fe}^{2+}$ ), the hydrogen ion concentration, and other variables<sup>9-12</sup>.

The magnetite formation shown in Fig. 1 consists of the reactions of both Eqs. (1) and (2). Equation (1) is a reaction to form fine magnetite nuclei, while Eq. (2) is a reaction to grow the thus-obtained magnetite nuclei. When the content of ferric chloride in the mixed iron chloride solution,  $\text{Fe}^{3+}/(\text{total Fe})$ , is varied, the number of nuclei generated by the reaction of Eq. (1) varies. This fact suggests that the specific surface area of the formed magnetite varies.

Because magnetite is easily oxidized and the ratio of Fe to oxygen is not fixed, hematite is generally used as the raw material for ferrite. In addition, magnetite is aggregated magnetically, thus homogeneous mixing with the other raw materials are impeded. To transform magnetite to hematite by thermal oxidation, the hematite-formation temperature was investigated by using thermal analysis and X-ray diffraction.

**Figure 2** shows the TG-DTA curve for magnetite particles. The peak of the DTA curve at 150°C indicated the transformation from magnetite to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). The peak at 480°C indicated the transformation from maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) to hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). If the hematite is heated at high temperature, hematite particles grow to become coarse ones. Therefore, the thermal oxidation should be carried out at lower temperature. Thus, from the result of DTA, the temperature of thermal

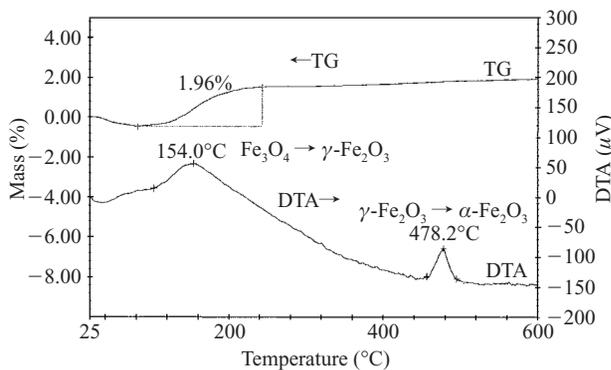


Fig.2 Thermal analysis data showing reactions during heating of  $\text{Fe}_3\text{O}_4$

oxidation in a range from 480°C to 500°C was selected. **Figure 3** shows the specific surface area of magnetite before the thermal oxidation and hematite after the thermal oxidation. A larger specific surface area of magnetite gives a larger specific surface area of hematite after thermal oxidation. It was found that a fine hematite having a specific surface area above  $1.0 \times 10^4 \text{ m}^2/\text{kg}$  was obtained by heating a magnetite, which have a specific surface area above  $1.5 \times 10^4 \text{ m}^2/\text{kg}$ .

In the process, however, since iron chloride and sodium hydroxide are used as the starting raw materials, a large quantity of Cl and Na are entrapped into the fine magnetite particles. **Figure 4** shows the relation between the Fe concentration in the mixed iron chloride solution before neutralization and the contents of Cl and Na in the obtained iron oxide. The content of ferric chloride in the mixed iron chloride solution,  $\text{Fe}^{3+}/(\text{total Fe})$ , was 10 mol%. The Cl concentration in the iron oxide was correlated with the concentration of mixed iron chloride solution before neutralization. Consequently, with higher concentration of iron chloride solution, a larger quantity of Cl was entrapped into the iron oxide. Conversely,

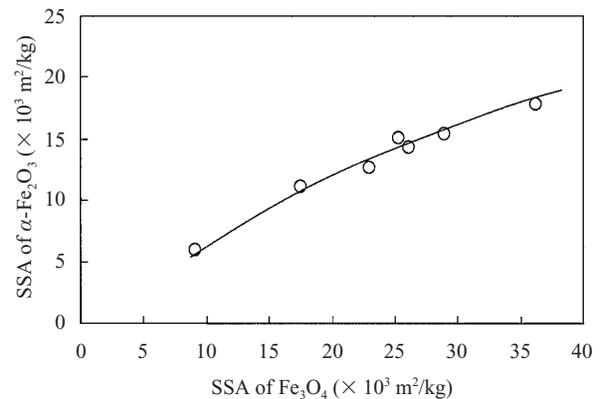


Fig.3 Relationship between SSA of  $\alpha\text{-Fe}_2\text{O}_3$  after heat treatment and SSA of  $\text{Fe}_3\text{O}_4$  before heat treatment

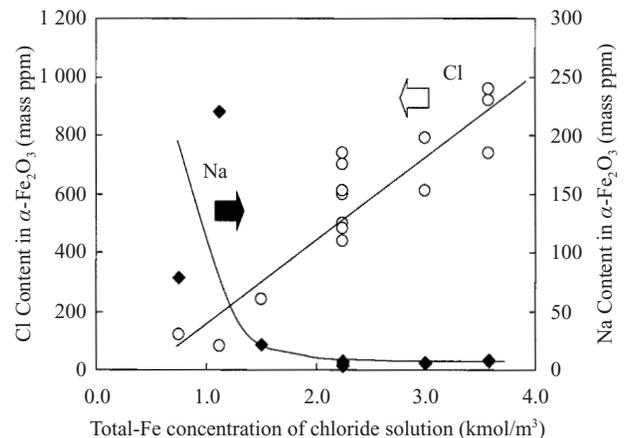


Fig.4 Effect of total-Fe concentration of ferrous and ferric chloride solution on contents of Na and Cl trapped in  $\alpha\text{-Fe}_2\text{O}_3$

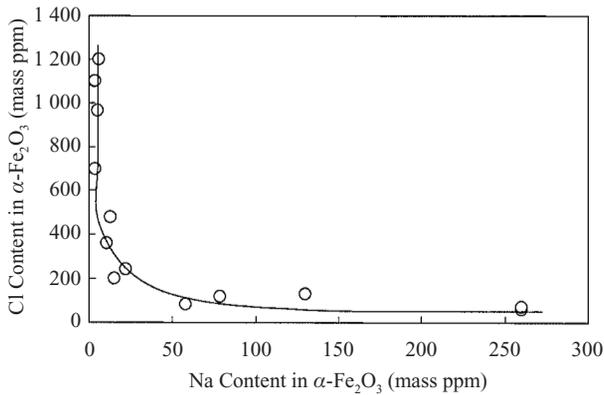


Fig.5 Relationship between Cl and Na contents in  $\alpha\text{-Fe}_2\text{O}_3$

if the concentration of the mixed iron chloride solution becomes lower, more Na is entrapped into the iron oxide.

**Figure 5** shows the relation between the Na concentration and the Cl concentration in the iron oxide. When the Cl concentration in the iron oxide was high, the Na concentration was low, and when the Na concentration was high, the Cl concentration was low. The entrapment of Cl and Na into the iron oxide is observed in the case of coprecipitation method of Eq. (1). The magnetite formation by air oxidation according to Eq. (2) does not show the entrapment of high concentration Cl and Na. Therefore, when magnetite nuclei are formed by the coprecipitation method, presumably Na and Cl are entrapped into the nuclei, or adsorbed onto the surface of nuclei. It is reported that, a large amount of Cl in the iron oxide, serves to decrease the spinel formation temperature of NiCuZn ferrites<sup>13-17</sup>. Cl in iron oxide, however, reacts with the electrode layer such as Ag in a chip inductor, which enhances the diffusion of Ag into the ferrite phase. It is also reported that the diffusion of Ag generates stress in ferrite and hence the magnetic properties deteriorate<sup>1</sup>. Another report<sup>13</sup> describes that a large amount of Na significantly decreases the initial permeability of ferrite. Consequently, unless the concentration of Cl and of Na, entrapped into the iron oxide, is stabilized at a low level, the ferrite properties vary significantly, which is unfavorable. Therefore, we investigated a method of reducing the concentration of Na and Cl.

**Figure 6** shows the relation between the hydrogen ion concentration of solution after completion of the magnetite formation and the Na concentration in the obtained magnetite. As seen in Fig. 6, when the hydrogen ion concentration of the solution was 6 or lower, the Na concentration in the iron oxide was low. In the case of hematite formation process by using ferric chloride solution, when the hydrogen ion concentration in the

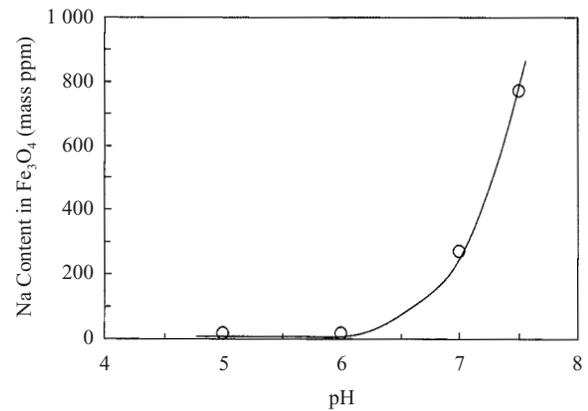


Fig.6 Relationship between Na content in  $\text{Fe}_3\text{O}_4$  and pH of solutions after the  $\text{Fe}_3\text{O}_4$  formation

solution decreases as the reaction progresses, the quantity of impurities eluted into the solution increases. A report<sup>4</sup>) describes the resulting decrease of the quantity of impurities in the iron oxide. This is presumably due to the phenomenon whereby the reduction of hydrogen ion concentration in the solution after the magnetite formation leads to the elution of Na, which then results in decreasing the Na concentration in the magnetite.

The authors focused on the tendency of decreasing Cl concentration shown in Fig. 5. That is, when a large quantity of Na is entrapped into the magnetite, Cl cannot be entrapped. By synthesizing the magnetite under the condition of Na-entrapping into the magnetite, the Cl concentration in the iron oxide decreases. By decreasing the hydrogen ion concentration in the solution after completion of the reaction to 6 or lower, the Na concentration decreases. With the synthesis conditions selected as described above, it was confirmed that both Cl and Na could be decreased.

### 3.2 Properties of Fine Iron Oxide Powder “JC-FH04”

**Photo 1** shows SEM images of fine iron oxide “JC-FH04” and conventional spray roasted iron oxide powder “JC-CPW.” Compared with JC-CPW, JC-FH04 had a small, uniform particle size. **Figure 7** shows the comparison of particle size distribution between JC-FH04 and JC-CPW. Compared with JC-CPW, JC-FH04 did not contain coarse particles, having a sharp particle size distribution. **Table 1** shows the specific surface area, purity, and quantity of impurities of JC-FH04 and JC-CPW. The specific surface area of JC-FH04 ranged from  $1.2 \times 10^4$  to  $1.8 \times 10^4$  m<sup>2</sup>/kg (average particle size from 60 to 100 nm), having higher values than those of JC-CPW. Regarding the impurities, JC-CPW contained Cl, coming from the starting materials, of about 700 ppm by mass at maximum, while JC-FH04 contained a smaller amount of Cl.

Table 1 Chemical composition and particle characteristics of JC-FH04 and JC-CPW

	XRD phase	SSA ( $\times 10^3 \text{ m}^2/\text{kg}$ )	Particle size ( $\mu\text{m}$ )	Purity (mass%) ( $\text{Fe}_2\text{O}_3$ )	Impurity levels (mass ppm)		
					$\text{SiO}_2$	Na	Cl
JC-FH04	$\alpha\text{-Fe}_2\text{O}_3$	12–18	0.06–0.1	99.5–99.7	< 120	< 40	< 200
JC-CPW	$\alpha\text{-Fe}_2\text{O}_3$	$\leq 5$	0.2–0.4	$\geq 99.3$	< 50	< 15	$\leq 700$

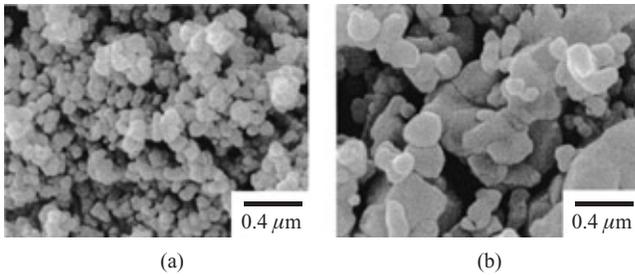


Photo 1 SEM photographs of (a) JC-FH04 and (b) JC-CPW

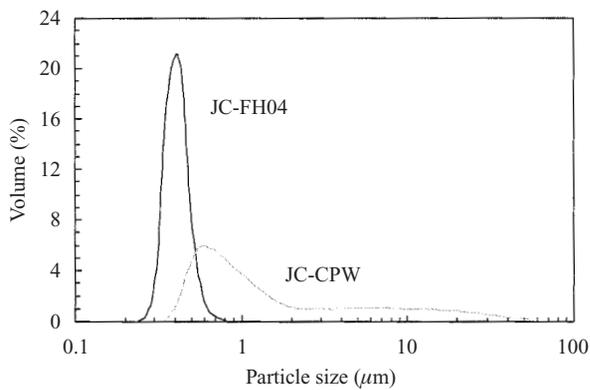


Fig.7 Particle distributions of JC-FH04 and JC-CPW

### 3.3 Properties of Ferrite Core Using Fine Iron Oxide Powder

Figure 8 shows the effect of iron oxide particle size and sintering temperature on sintered density of NiCuZn ferrites. By using fine iron oxide powder, a high sintered density above  $5.1 \times 10^3 \text{ kg/m}^3$  was obtained at a sintering temperature of  $900^\circ\text{C}$ . The result shows that JC-FH04 is superior in sintering performance to JC-CPW. Figure 9 shows the dependency of initial permeability  $\mu_i/\mu_0$  of NiCuZn ferrites, measured at room temperature and at a frequency of 100 kHz, on the sintering temperature. The initial permeability  $\mu_i/\mu_0$  was increased by using the fine iron oxide powder than that of JC-CPW even when sintered at  $900^\circ\text{C}$  or below.

The mechanism for the low temperature sintering of fine iron oxide powder was investigated. Photo 2 shows SEM images of ferrite mixed powder, calcined powder, and milled powder using fine iron oxide powder and JC-CPW. With the mixed powder using fine iron oxide powder, homogeneous iron oxide particles contain dispersed coarse particles of NiO, ZnO, and CuO. In the calcined powder and milled powder, these coarse par-

ticles, observed in the mixed powder, vanished to give uniform particles. This means that during the calcination process NiO, ZnO, and CuO diffused into the main raw material iron oxide to form the NiCuZn ferrites phase. On the other hand, in the mixed powder, the calcined powder, and the milled powder using JC-CPW, the particles were totally coarse and nonuniform compared with the case of fine iron oxide powder. The phenomenon was presumably caused by the shape of iron oxide as the main raw material. The particle size and its distribution of calcined powder were found to strongly dependent on the particle distribution of iron oxide powder as the main raw material. By using fine and uniform particle size of fine iron oxide powder as the starting raw material, fine and uniform calcined powder can be obtained. As a result, milling of short duration produces fine particles and so improves the sinterability, thereby presumably allowing sintering at lower temperatures.

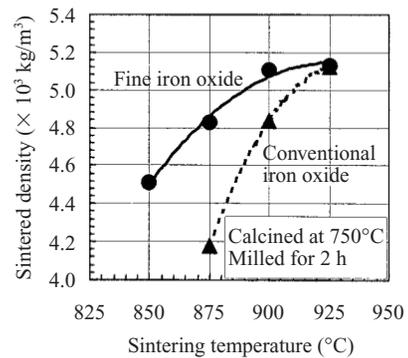


Fig.8 Effects of iron oxide particle size and sintering temperature on sintered density of NiCuZn ferrite

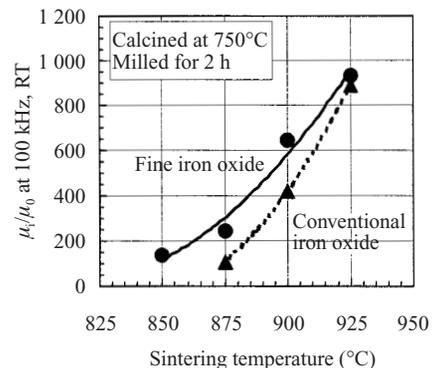


Fig.9 Comparison of  $\mu_i/\mu_0$  of NiCuZn ferrites of fine and conventional iron oxide ( $\mu_0$ : Permeability of vacuum)

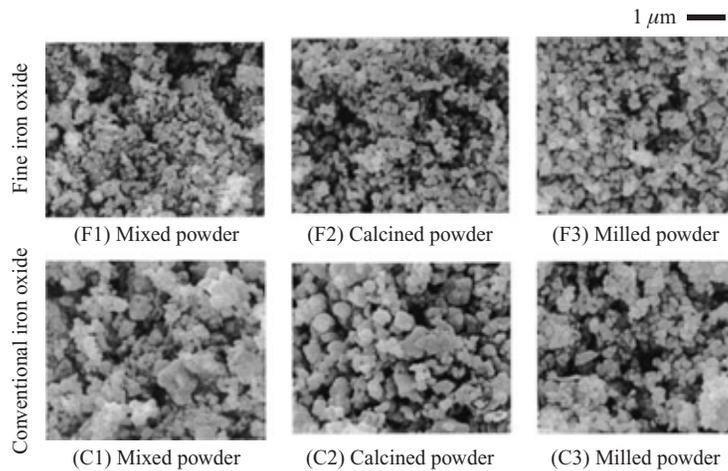


Photo 2 SEM photographs of mixtures, calcined powders and milled powders made from fine and conventional iron oxides

#### 4. Conclusions

The manufacturing conditions of fine iron oxide powder were investigated. Using ferrous chloride solution generated from ironmaking plant as the main raw material, and applying the method of heating magnetite synthesized by the wet process, the following results were obtained.

- (1) By varying the mixing ratio of ferrous chloride to ferric chloride, the particle size of magnetite could be controlled. By increasing the mixing ratio of ferric chloride, fine particles of magnetite could be obtained.
- (2) By heating magnetite fine particles, hematite fine particles having a specific surface area above  $1 \times 10^4 \text{ m}^2/\text{kg}$  could be obtained.
- (3) The amount of Na and Cl could be decreased by synthesizing magnetite under a condition to entrap Na, and decreasing the pH of solution after completing the reaction to 6 or lower.
- (4) Compared with the iron oxide powder manufactured by the conventional spray-roasting process, the fine iron oxide powder JC-FH04 has small average particle size, uniform particle size distribution, and small concentration of Cl coming from the starting raw materials.
- (5) By using fine iron oxide powder as the raw material for ferrite,  $5.1 \times 10^3 \text{ kg/m}^3$  of sintered density and high initial permeability even under sintering at a low temperature of  $900^\circ\text{C}$  could be achieved. Compared with the iron oxide manufactured by the conventional spray-roasting process, the fine iron oxide powder could be sintered at lower temperature.

These results revealed that the developed JC-FH04 has excellent properties as the raw material iron oxide for NiCuZn ferrite, especially for multilayer chip induc-

tors which specifically require co-firing with the electrode layer. JC-FH04 is expected to enable the production of smaller multilayer chip inductors with greater functionality.

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