High Temperature Measurement of Complex Permittivity and Permeability of Fe$_3$O$_4$ Powders in the Frequency Range of 0.2 to 13.5 GHz

Masahiro HOTTa,1) Miyuki HAYASHI1) and Kazuhiro NAGATA2)

1) Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552 Japan. 2) Department of Conservation Science, Tokyo University of the Arts, 12-8 Ueno Koen, Taito-ku, Tokyo 110-8714 Japan.

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The real and imaginary parts of relative permittivity ($\varepsilon'_r$ and $\varepsilon''_r$) and permeability ($\mu'_r$ and $\mu''_r$) of Fe$_3$O$_4$ powder were successfully measured over the temperature range of 25–575°C by means of the coaxial transmission line method in order to elucidate the heating behaviours of Fe$_3$O$_4$ powder. The measurement frequency range is from 0.2 to 13.5 GHz. With respect to the temperature dependencies of the complex permittivity, the $\varepsilon'_r$ values show a peak around 450–500°C. The $\varepsilon''_r$ values monotonically increase with increasing temperature, in particular, showing abrupt increase above ca. 400°C. As for the complex permeability, the $\mu'_r$ values decrease with an increase in temperature, and reach the same level as that of vacuum ($\mu'_r$=1) at 575°C, i.e., the maximum measurement temperature. The $\mu''_r$ values increase with temperature until 500°C below 3.5 GHz although they monotonically decrease with an increase in temperature above 3.5 GHz.

KEY WORDS: Fe$_3$O$_4$; high temperature; permittivity; permeability; coaxial transmission line method; Curie temperature.

1. Introduction

It is a worldwide consensus that CO$_2$ emission reduction and energy conservation are urgent tasks for the prevention of global warming. The strategy for this issue could be conversion of conventional energy utilization system into new one and/or promotion of the use of new energy, that is, enlargement of the use of non-fossil fuels such as nuclear power, solar power, wind power and so on. As for iron making, high temperature combustion gas is used to heat raw materials so far. We have been examining the possibility of the usage of microwaves as an alternate heating source for ironmaking.$^{1-4)}$

Microwaves are electromagnetic waves, the frequency range of which is from 0.3 to 300 GHz (corresponding to wavelengths ranging from 1 mm to 1 m). Microwave heating has a number of advantages over more conventional heating methods.$^{5)}$ Microwave energy dissipates instantaneously throughout the volume of the material and heats it directly. Materials with high absorbency of microwave energy are heated selectively. In fact, magnetite and carbon are excellent absorbers of microwave energy while refractory materials are relatively lower absorbers. Recently, it has been found that microwave (2.45 GHz) can fully sinter a large size of powdered metallic and ceramic materials although bulk metal and ceramic cannot be heated by microwave as is well known.$^{6)}$ This indicates that microwave is suitable for heating powder iron ore. This feature of microwave is a big advantage for ironmaking because the usage of powder iron ore instead of lump ore causes reduction reaction more rapidly. Ishizaki et al.$^{2)}$ have successfully produced the highly-pure pig iron from a carbon composite iron ore pellet composed of the mixture of magnetite ore and coal powders by means of a 2.45 GHz multi mode microwave furnace, and have reported that the temperature reaches 1350°C only 500 s after the onset of microwave power of 3 kW. The produced pig iron contains lower concentrations of Si and P than the pig iron produced by blast furnace. The lower impurity concentrations may be associated with the higher oxygen partial pressures in a carbon composite iron ore pellet, which could be caused by the rapid heating of raw materials.$^{7)}$ In fact, one of the important features of microwave heating is the rapid heating.

Microwave absorption can be described by the following equation.

$$P = \frac{1}{2} \sigma |E|^2 + \pi f \varepsilon''_r |E|^2 + \pi f \mu''_r |H|^2$$

Where $|E|$ electric field amplitude, $|H|$ magnetic field amplitude, $\sigma$ electrical conductivity, $f$ microwave frequency, $\varepsilon''_r$ imaginary part of relative permittivity, $\mu''_r$ imaginary part of relative permeability. The first, the second and the third terms of the right hand side of Eq. (1) correspond to the microwave absorptions due to the Joule loss, the dielectric loss and the magnetic loss, respectively. In order to elucidate the heating behaviors of raw materials, the authors
measured the complex permittivity and permeability of Fe₃O₄ powders having various particle sizes at room temperature as a function of microwave frequency so as to search for the optimal condition regarding the microwave ironmaking.⁸ It has been found that the imaginary part of complex permeability of Fe₃O₄ powder with a particle size of 50 nm–180 mm show the peaks in the frequency range of 0.706 to 2.99 GHz, depending on the particle size. It has also been found that the imaginary part of complex permittivity of Fe₃O₄ powder is quite large having a peak around 10 GHz. To the best of the authors’ knowledge, however, there is no previous report with regard to the complex permittivity and permeability of Fe₃O₄ at elevated temperatures although such data are strongly required to clarify the microwave heating behaviors of raw materials at high temperatures.

There are some reports with respect to the complex permittivity and permeability measurements at high temperatures. Most of all reports are summarized in Table 1,⁹–¹⁴ which shows targeted substances, types of measurement techniques, measurement temperature and frequency ranges, and types of observed data. The adopted techniques can be categorized into two; resonance cavity and coaxial probe. As for the resonance cavity, complex permittivity and/or permeability can be measured with a high degree of accuracy at a single frequency. On the other hand, the coaxial probe enables us to measure the frequency dependency of complex permittivity although complex permeability cannot be measured by the same method. In the present study, the authors chose the coaxial transmission line method to measure the complex permittivity and permeability of Fe₃O₄ powders at high temperatures up to around the Curie temperature (585°C)¹⁵ because it allows us to measure permeability as well as permittivity as a function of frequency.

2. Experimental
2.1. Sample Characteristics
Fe₃O₄ powder (99.9% purity, Kojundo Chemical Laboratory Co., Japan) having a particle size of 38–62 μm sorted by mesh control was subjected to the high temperature permittivity and permeability measurements. According to our previous study,⁸ the εᵣ values of acicular Fe₃O₄ powders are about 4 times larger than those of spherical powders. Thus, it is likely that the shape and/or the surface area of the powders affect the εᵣ values. Therefore, the morphology of the powders was determined by scanning electron microscopy (SEM) (Shimadzu Co., EPMA1610) Fig. 1 shows a SEM image of powders. It can be seen that the particles have spherical shape. The specific surface area of the powders was also measured by the gas adsorption method (Shimadzu Co., TriStar3000) using N₂ gas. The specific surface area has been obtained to be 0.34 m²/g, which is about 10 times larger than the surface area calculated assuming that the particle is a smooth sphere with a density of 5.03 g/cm³. This may correspond to the fact that the surface of the powder is rough, as shown in Fig. 1.

2.2. Measurement Apparatus
The real and imaginary parts of relative permittivity (εᵣ' and εᵣ″) and permeability (μᵣ' and μᵣ″) were measured over the temperature range of 25–575°C by the coaxial transmission line method using a network analyzer (Agilent Technologies, N5230A), coaxial cables and a APC7 type coaxial sample holder over the microwave frequency range between 0.2 and 13.5 GHz. Figure 2 shows the schematic illustration of the apparatus. Sample holder is made of SUS316-L grade stainless steel and the holder length is 300 mm. A K type thermocouple was tied to the sample holder using Pt wire.

In this experiment, temperatures were measured by a thermocouple attached to the outer wall of the holder instead of a thermocouple embedded in the sample. Therefore, the measurement temperatures are apparent ones and should be calibrated to obtain the true temperatures. To calibrate the temperatures, the apparent and true temperatures were simultaneously measured by the thermocouples attached to the outer wall of the holder and embedded in the sample, respectively, during the heating cycle. The heating
argon gas, from which oxygen was removed in advance by passing the gas through magnesium turnings at 500°C, was flowed in the silica tubes to prevent Fe₃O₄ powder as well as the inside wall of the stainless steel sample holder from oxidation. Oxidation of the inside wall of the sample holder disables the measurement.

The temperature was increased with a heating rate of 15°C/min during the measurements. The transmission and reflection (S-parameter) of the irradiated microwave were measured about every 1°C during a heating cycle. The output power of the network analyzer was ca. 1 mW. Each measurement was carried out over the frequency range between 0.2 and 13.5 GHz spending about 2 s.

The complex permittivity and permeability were calculated by the algorithm of Nicolson–Ross model[16,17] using S-parameters. It was confirmed by X-ray diffraction analysis that the powder samples were only composed of Fe₃O₄ before and after the measurement.

3. Results

Figure 4 shows the real and imaginary parts of relative permeability (µᵣ and µᵢ) and permittivity (εᵣ and εᵢ) of the Fe₃O₄ powders having a particle size of 38–62 μm and a relative density of 62.9% as a function of frequency f and temperature T.

3.1. Frequency Dependency of the Complex Permittivity and Permeability of the Fe₃O₄ Powder

Figure 5 shows the frequency dependency of the real and imaginary parts of relative permeability and permittivity at 25, 285 and 575°C.

It can be seen from Figs. 4 and 5 that the values of the relative complex permittivity and permeability are a little fluctuating, which may be due to experimental errors. The µᵣ values monotonically decrease with increasing frequency over the measurement frequency and temperature ranges. The µᵢ values show a peak around 2.5 GHz below 90°C, and monotonically increase with decreasing frequency above 2.5 GHz. The εᵣ values are almost constant over the measurement frequency ranges below 350 and 520°C, respectively. Above 350°C, the εᵢ values abruptly increase with decreasing frequency below ca. 2 GHz, as shown in Fig. 5(i). In contrast, the εᵢ values show a large decrement above ca. 520°C at almost the same frequency as the one at which the εᵢ values show a large increment. Previously, the authors have measured the values of µᵣ, µᵢ, εᵣ, and εᵢ for powder and bulk SiO₂ at room temperature in the frequency range between 0.2 and 13.5 GHz, and have found that the values at lower frequencies are considered to contain large errors as demonstrated by the large standard deviations in the values of µᵣ, µᵢ, εᵣ, and εᵢ of the bulk sample. Therefore, it could be considered that the abrupt changes in the εᵢ values below ca. 2 GHz above 350 and 520°C are also associated with the experimental errors. The µᵣ and µᵢ values at lower frequencies could also contain large errors.

3.2. Temperature Dependency of the Complex Permittivity and Permeability of the Fe₃O₄ Powder

Figure 6 shows the real and imaginary parts of relative
permeability \((\mu_r'\text{ and } \mu_r'')\) and permittivity \((\varepsilon_r'\text{ and } \varepsilon_r'')\) of Fe\(_3\)O\(_4\) powders having a particle size of 38–62 \(\mu\)m and a relative density of 62.9% as a function of frequency \(f\) and temperature \(T\).

It can be seen from Fig. 6 that the \(\mu_r'\) values decrease with an increase in temperature, and reach the same level as that of vacuum \((\mu_r'=1)\) at 575°C, i.e., the maximum measurement temperature. The \(\mu_r''\) values increase with temperature until 500°C below 3.5 GHz although they monotonically decrease with an increase in temperature above 3.5 GHz. With respect to the temperature dependencies of the complex permittivity, the \(\varepsilon_r'\) values show a peak around 450–500°C. The \(\varepsilon_r''\) values monotonically increase with increasing temperature, in particular, showing abrupt increase above ca. 400°C. To confirm the reproducibility of the temperature dependencies, the relative complex permeability and permittivity were also measured with a heating rate of 2°C/min. The relative density was 44.0%. The temperature dependencies of the values of \(\mu_r'\), \(\mu_r''\), \(\varepsilon_r'\), and \(\varepsilon_r''\) resemble those measured with a heating rate of 15°C/min, as shown in Fig. 7.

4. Discussion

4.1. Confirmation of the Feasibility of the Measurement

The authors have previously measured the \(\varepsilon_r'\) values of powder and bulk SiO\(_2\) at room temperature using a 10 mm coaxial sample holder (KEAD CSH-APC7)\(^8\) and have found that the relation of the values at 5.8 GHz to the relative density for SiO\(_2\) are in good agreement with that reported by Inoue \textit{et al.}\(^{18}\). In order to confirm the feasibility of the present experiment using a 300 mm sample holder developed for high temperature measurements, the data measured by a 300 mm holder at room temperature were compared with the data measured by a 10 mm holder.

\(\text{Figure 8}\) shows the frequency dependency of the complex permeability and permittivity of Fe\(_3\)O\(_4\) powders with a...
particle size of 38–62 mm at room temperature. The values previously measured using a 10 mm coaxial sample holder are also included in this figure. Figure 9 shows the values of $\mu_r'$, $\mu_r''$, $\varepsilon_r'$, and $\varepsilon_r''$ at 2.45 GHz as a function of the relative densities of Fe$_3$O$_4$. The values measured using a 10 mm sample holder are also included in this figure. In Fig. 9, the $\mu_r'$ and $\mu_r''$ values are the data for the powders with a particle size of 38–62 $\mu$m although the $\varepsilon_r'$ and $\varepsilon_r''$ values are the data for the powders with various particle sizes ranging from 50 nm to 180 $\mu$m and bulk Fe$_3$O$_4$ samples. This is because the $\varepsilon_r'$ and $\varepsilon_r''$ values vs. frequency curves are almost identical irrespective of the particle size, while the $\mu_r'$ and $\mu_r''$ values vs. frequency curves are dependent on the particle size. The frequency at the peak of the $\mu_r''$ vs. frequency curve decreases with an increase in the particle size of Fe$_3$O$_4$ sample.

It can be seen from Fig. 8(a) that the $\mu_r'$ values monotonically decrease with an increase in frequency. The values are a little larger than those measured by a 10 mm holder. The difference in the $\mu_r'$ values is due to the difference in the relative densities, as shown in Fig. 9(a). As for the $\mu_r''$ values in Fig. 8(b), the frequency at the peak of the $\mu_r''$ vs. frequency curve is around 2.5 GHz, which is in excellent agreement with those for the data measured by a 10 mm holder. The difference in the $\mu_r''$ values is due to the difference in the relative densities, as shown in Fig. 9(b). The authors have reported that the $\varepsilon_r''$ values measured by a 10 mm holder show a peak around 10 GHz just below which the $\varepsilon_r'$
values show a slight decrement. The \( \varepsilon_r'' \) values measured by a 300 mm holder also show a peak around 10 GHz although the peak is subtle. In fact, some peaks observed by a 10 mm holder were also small. The authors have not clarified yet which factors affect the height of the peak around 10 GHz. Inspection of Figs. 9(c) and 9(d) reveals that the \( \varepsilon_r' \) and \( \varepsilon_r'' \) values measured by a 300 mm holder are consistent with the values obtained using a 10 mm holder. Consequently, the data measured at room temperature using a 300 mm sample holder are considered to be reasonable, which may establish the feasibility of the present experiment at room temperature.

The feasibility of the present experiment at high temperature can be demonstrated by the fact that the \( \mu_r' \) values reach the same level as that of vacuum (\( \mu_r'=1 \)) at 575°C, as shown in Fig. 6, which is in vicinity of the Curie temperature of Fe\(_3\)O\(_4\) (585°C). However, the \( \mu_r'' \) values are ca. 0.5 above 10 GHz just below the Curie temperature, i.e. 575°C, and are even larger as the frequencies become smaller although the magnetic loss (\( \mu_r'' \)) should be zero above the Curie temperature. The reason the \( \mu_r'' \) values are not zero above the Curie temperature has not been clarified yet.

4.2. Microwave Heating Mechanisms of Fe\(_3\)O\(_4\) Powder

As described in introduction section, microwave absorptions are composed of the Joule loss, the dielectric loss and the magnetic loss. For dielectric materials, the dielectric loss and the magnetic loss are relevant to the \( \varepsilon_r' \) and \( \mu_r' \) values, respectively. The Joule loss is due to the current induced by the electric field and/or the eddy current induced by the magnetic field, total current density \( J \) is expressed by the following equation

\[
J = \sigma E + \frac{\partial (\varepsilon_r' E)}{\partial t} = j \sigma \varepsilon_0 \left( \varepsilon_r' - \frac{\sigma}{\omega \varepsilon_0} \right) E \quad \text{......(2)}
\]

where \( \sigma \) electric conductivity of material, \( \varepsilon_0 \) permittivity of vacuum, \( \omega \) angular frequency. Since the relative complex permittivity is

\[
\varepsilon_r^+ = \varepsilon_r' - j \varepsilon_r'' \quad \text{.................(3)}
\]

where \( \varepsilon_r' \) and \( \varepsilon_r'' \) are the real and imaginary parts of relative permittivity, the electric conductivity \( \sigma \) is

\[
\sigma = \omega \varepsilon_0 \varepsilon_r'' \quad \text{.................(4)}
\]

Therefore, for conductive materials, the Joule loss is also relevant to the \( \varepsilon_r' \) value.

As shown in Fig. 6, the \( \mu_r'' \) values are around 2 and increase with temperature until 500°C below 3.5 GHz. This indicates the possibility that at lower frequencies, the temperature of the Fe\(_3\)O\(_4\) powder increase owing to the magnetic loss below the Curie temperature. On the other hand, the \( \varepsilon_r'' \) values monotonically increase with increasing temperature, and in particular, show abrupt increase above ca. 400°C. In fact, Fe\(_3\)O\(_4\) is composed of Fe\(^{3+}\) and Fe\(^{2+}\) ions and electrons ‘hop’ between these ions, yielding electric conduction. The hoping of electrons becomes more active and the electric conductivity becomes larger as temperature increases, which corresponds to the increase in the \( \varepsilon_r'' \) values. The obtained temperature dependencies of the \( \varepsilon_r'' \) values may indicate that Fe\(_3\)O\(_4\) powder is more dielectric below ca. 400°C and more conductive above ca. 400°C. As a consequence, it is considered that the Fe\(_3\)O\(_4\) powder can be continuously heated by the combination of the magnetic loss at lower temperatures and the Joule loss at higher temperatures. However, Miles et al. have reported that the direct current conductivity of Fe\(_3\)O\(_4\) remains constant around 400°C, which is in conflict with our prediction. Accurate electric conductivity measurements of Fe\(_3\)O\(_4\) are in progress in Department of Chemistry and Materials Science, Tokyo.
5. Conclusions

The real and imaginary parts of relative permittivity ($\varepsilon'_r$ and $\varepsilon''_r$) and permeability ($\mu'_r$ and $\mu''_r$) of Fe$_3$O$_4$ powder with a particle size of 38–62 μm were successfully measured over the temperature range of 25–575°C by means of the coaxial transmission line method. The obtained results are summarized as follows.

(1) With respect to the temperature dependencies of the complex permittivity, the $\varepsilon'_r$ values show a peak around 450–500°C. The $\varepsilon''_r$ values monotonically increase with increasing temperature, in particular, showing abrupt increase above ca. 400°C. As for the complex permeability, the $\mu'_r$ values decrease with an increase in temperature, and reach the same level as that of vacuum ($\mu'_r = 1$) at 575°C, i.e., the maximum measurement temperature. The $\mu''_r$ values increase with temperature until 500°C below 3.5 GHz although they monotonically decrease with increase in temperature above 3.5 GHz.

(2) The data measured at room temperature by a 300 mm length sample holder developed for high temperature measurements are in good agreement with the data measured by a 10 mm length commercial sample holder. This as well as the fact that the $\mu'_r$ values become unity in the vicinity of the Curie temperature may establish the feasibility of the present experiment to some extent.

(3) The temperature dependencies of the $\mu''_r$ and $\mu''_r$ values demonstrate that the Fe$_3$O$_4$ powder can be continuously heated by the combination of the magnetic loss at lower temperatures and the Joule loss at higher temperatures.

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