Coupling of Magnetite Particles with Microwaves at Temperatures lower than the Curie Point

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Abstract

Effect of the particle size \((d)\) and apparent density on the coupling of microwaves with \(\text{Fe}_3\text{O}_4\) was investigated at temperatures lower than the Curie point, \(T_c \approx 585 \, ^\circ\text{C}\). Two samples in the form of tablet with particle sizes of 45-75 \(\mu\text{m}\) (MT75) and <45 \(\mu\text{m}\) (MT45) and one sample in the form of powder with a particle size of <45 \(\mu\text{m}\) (MP45) were heated in multi-mode and maximum E- and H-field modes using a microwave generator at a frequency of 2.45 GHz. According to the results, an earlier temperature increase and also a higher temperature was achieved in the sample heated in the maximum H-filed mode. Regarding the incubation time in all samples, the particle size of \(\text{Fe}_3\text{O}_4\) has no significant effect on the time required for the initial temperature increase in the presence of the H-field. In the maximum E-field mode, a shorter time was required for the temperature increase in the MT75 sample than MT45. At \(T \leq T_c\), magnetic loss and Joule loss are the dominant heating mechanisms in the presence and absence of the H-field, respectively. Magnetic loss is independent of the particle size whereas Joule loss which is influenced by electrical conductivity, affected by particle size. Therefore, above-mentioned effect of the particle size is attributed to the dominant heating mechanism. Also, some of the small particles seems to be transparent owing to a greater penetration depth \((\delta)\), ca. 80 \(\mu\text{m}\), at room temperature causing an earlier onset of temperature increase in sample with larger particle size, MT75. Moreover, microwave absorption in a sample with higher apparent density, MT45, was lower because of a higher electrical conductivity of sample in tablet form, MT45, than powder form, MP45.

Key words: Magnetite; Microwave absorption; Particle size; Apparent density; Curie point;

1. Introduction

Iron production with microwave heating is considered a possible solution to mitigate the CO\(_2\) emission. Reduction of iron oxide using highly efficient microwave heating is reported as a new method for energy conservation and also for decreasing the CO\(_2\) emission [1–3]. For a more efficient use of the microwave irradiation, it is important to understand the heating mechanism and also find effective parameters for the microwave heating of powdery materials. Microwave power absorption by materials, \(P\) (W/m\(^3\)), can be evaluated by Eq. (1) which is directly related to the penetration depth, \(\delta\) (m). Penetration depth presents the distance from the surface to a point inside the materials where the power of the exposed electromagnetic waves decreases to 1/e, 36.8\%, of the surface value [4,5] which can be calculated according to Eq (2) [4]:

\[
P = \frac{1}{2} \sigma |E|^2 + \pi f \varepsilon_0 \varepsilon' |E|^2 + \pi f \mu_0 \mu' |H|^2
\]

\[
\delta = \left[ \frac{\omega_0^2 \varepsilon' \mu'}{2} \left( \frac{\sigma^2}{\omega_0^2 \varepsilon'^2 - 1} \right) \right]^{\frac{1}{2}}
\]

where \(\sigma\) (S/m) is the electrical conductivity, \(E\) (V/m) is the electric field amplitude, \(H\) (A/m) is the magnetic field amplitude, \(f\) (Hz) is the microwave frequency, \(\varepsilon_0\) (F/m) and \(\mu_0\) (N/A\(^2\)) are the permittivity and permeability of vacuum, respectively. \(\varepsilon'\) (dimensionless) and \(\mu'\) (dimensionless) are the imaginary part of permittivity and permeability, respectively. \(\varepsilon\) and \(\mu\) are the real part of permittivity and permeability, respectively. According to Eq. (1), three different mechanisms including Joule loss (first term, W/m\(^3\)), dielectric loss (second term, W/m\(^3\)), and magnetic loss (third term, W/m\(^3\)) would contribute to microwave heating. Hayashi et al. [4] observed that microwave absorption of magnetite at the steady state hardly depends on the particle size and theorized that it is because of the great penetration depth of \(\text{Fe}_3\text{O}_4\), ca. 80 \(\mu\text{m}\), at room temperature at 2.45 GHz. However, such large penetration depth should be considered in the case of interaction between \(\text{Fe}_3\text{O}_4\) and microwaves at temperatures lower than the Curie point, ca.
585 °C [4]. At the steady state, the penetration depth would be significantly shallower than 80 μm due to an increase in the conductivity with temperature. Moreover, no sufficient information is available about initial stages of temperature increase during microwave heating. In fact, microwave absorption at the steady state is related to higher temperatures whereas initial stages of temperature increase depend on the low-temperature (T< 585 °C) interaction between the microwaves and materials. In this study, the effect of the apparent density and particle size on the microwave absorptivity of Fe3O4 is investigated by focusing on the initial stages of temperature increase for a better understanding of the interaction between the microwaves and materials at temperatures lower than the Curie point.

2. Experimental Procedure

2.1. Sample preparation

Three types of magnetite samples were prepared as follows:

Magentic powder (ca. 1 μm, purity of 99%) was pressed into a briquette shape (diameter, 30 mm; thickness, 20 mm) at a pressure of 42 MPa and then heated under a flow of Ar at 1350 °C for 1 h in an electric resistance furnace. The heat-treated briquettes were crushed and ground to a certain grain size, as mentioned above. To prepare the tablet samples, 0.02 g of a 5 mass% solution of polyvinyl alcohol in water was added as a binder to 3 g of the crushed magnetite powder. Cylindrical tablet shape samples (diameter, 15 mm and thickness, 5 mm) were formed by cold-pressing followed by drying at 120 °C for 10 h. The properties of the samples are presented in Table 1. The apparent density of the tablet shape sample was calculated by dividing the weight of the sample by its apparent volume (height×π×[radius]²) at 25 °C and pressure of 1 atm. To evaluate the density of the powder sample, 3 g of the powder was loaded into a 2.5 mL graduated cylinder followed by vibrating for 3 min using an ultrasonic cleaner (USM, AS ONE, JAPAN). Then, the bulk density of the powder sample was calculated by dividing the mass (g) of the powder, 3 g, by the volume occupied in the cylinder [6]. The electrical conductivity of the tablet shape samples was evaluated using an Analog tester (CX-270N, Custom) at 25 °C. The average electrical conductivity of the sample was calculated from the electrical conductivity along two directions: Along the pressure direction and orthogonal to the pressure direction. To evaluate the electrical conductivity of the powder sample, 3 g of each sample was loaded into a silica tube (20.6 mm outer diameter (OD), 15.4 mm inner diameter (ID), and 35.5 mm height). Then, the conductivity was measured between the two end of the tube occupied by the sample using an Analog tester (CX-270N, Custom) at 25 °C.

2.2. Microwave heating

The samples were subjected to microwave irradiation under multi- (whereby both the magnetic field (H) and the electric field (E) perpendicular to it contribute to heating) and single-mode operation using a microwave generator with a maximum output power of 1.5 kW at 2.45 GHz under N2 atmosphere. For microwave heating under each mode (multi- and single-), a specific cavity was designed by the manufacturer. Typically, the sample was loaded in an alumina crucible (41 mm OD, 36.5 mm ID, and 49 mm height) surrounded by ceramic wool and covered with an insulating ceramic brick. The crucible was placed in a quartz chamber (95 mm OD, 85 mm ID, 96 mm height) and the sample was protected from oxidation by flowing N2 during the experiments. The ceramic wool and insulation fibre, which do not absorb microwaves, served as thermal insulators preventing heat loss during heating as well as protectors of the quartz chamber. In case of the single mode, the H- or E-field has maximum amplitude, whereas the amplitude of the other is ca. 0. For heating in the single-mode, a cavity was used different from that of the multi-mode one. An adjusting plunger was used to define the maximum magnetic or electric field position. The sample was placed on a piece of ceramic fibre and placed inside a quartz tube, and it was protected from oxidation by flowing N2 during the experiments. A constant power of 1050 W was manually set using three tuning stubs until the end of the heating process in all the experiments. The temperature of the sample was measured through a window above the sample using an infrared radiation thermometer. The measurement temperature range is 330–1500 °C.

3. Results and Discussion

3.1. Effect of particle size

According to the heating patterns of the samples in form of tablet shape shown in Fig. 1, an earlier temperature increase and a higher temperature during treatment was observed in the sample heated in the maximum H-filed mode compared to the multi-mode and maximum E-filed mode. In case of heating in the maximum H-field mode, the temperature increased rapidly to ca. 690 °C via the magnetic loss mechanism and then increased gradually at a lower rate to ca. 1020 °C. The magnetic loss does not contribute to the heating at temperatures higher than the Curie point [4,7] and an increase in the electrical conductivity due to the temperature increase [4] would be the reason for the increase in the temperature of the sample via Joule loss, regarding Eq. (1). The incubation time for temperature increase in samples MT75 and MT45, during treatment in the multi-mode, maximum E- and H-field modes are shown in Fig. 2. This result indicates that in the presence of H-field, where the magnetic loss is the dominant mechanism for heating at temperatures lower than the Curie point, ca. 585 °C [4], microwave heating is not affected by particle size of the sample. This is possibly due to the permeability, which is independent of the particle size, as reported by Hotta et al. [8].

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Table 1: Properties of magnetite samples.

| Sample No. | MP45   | MT45   | MT75   |
|------------|--------|--------|--------|
| Particle size (μm) | < 45   | < 45   | 45-75  |
| Form       | Powder | Tablet | Tablet |
| Apparent density (g/cm$^3$) | 2.1    | 3.3    | 3.3    |
| Average $\sigma$ at 25 °C (S/cm) | $^a$ 1.6×10$^{-4}$ | 2.0×10$^{-4}$ |

$^a$ The value is lower than the measurement limitation of ca. 8.3 × 10$^{-8}$ S/cm.

In the absence of a high H-field at temperatures lower than the Curie point, neither magnetic loss nor dielectric loss can contribute to microwave heating and only Joule loss would be an effective mechanism for heating, according to Eq. (1). It seems that the Joule loss of sample MT75 is higher than that of MT45 because of the higher electrical conductivity of the sample with a larger particle size, as presented in Table 1. In addition, a greater penetration depth is expected owing to a significant decrease in $\mu'$ in the maximum E-field mode, according to Eq. (2), which would affect its microwave absorption. It has been reported that the ratio of the particle size ($d$) to the penetration depth ($\delta$) is a critical factor for optimum microwave absorption by conductive materials [5,9]. For a very low $d/\delta$ ratio, the particle acts as a transparent material and cannot couple with the microwaves. For a very high $d/\delta$ ratio, most of the microwaves will be reflected and the sample cannot heat well. For instance, a $d/\delta$ ratio of ca. 2.4 is suggested for maximum microwave absorption in nonmagnetic metal particles [5,9]. Thus, larger particles can absorb more of the microwave power owing to their higher $d/\delta$ ratios whereas some of the smaller particles cannot couple with the microwaves and behave like a transparent material, owing to their low $d/\delta$ ratio.

It seems that most of the particles in sample MT45 fall in the transparent region at temperatures lower than the Curie point, whereas the particles in samples MT75 fall in the absorption region for the same temperature range. Therefore, an early onset of temperature increase in sample MT75 compared to the onset of temperature increase of sample MT45 would be due to both higher Joule loss and higher $d/\delta$ ratio of the sample with a larger particle size, MT75. This result proves the considerable impact of the particle size on microwave absorption at temperatures lower than the Curie point.

### 3.2. Effect of the apparent density

To investigate the effect of the apparent density on the initial stages of temperature increase during the microwave heating, each experiment was conducted at least twice and the average time required for the initial temperature increase for each sample is plotted in Fig. 3, with the standard deviation represented as error bars.

A shorter time was required for the initial temperature increase in sample MP45, indicating better microwave absorption by this sample compared to sample MT45 even at low temperatures.

For acicular magnetite powders at room temperature and a frequency of 2.45 GHz, $\delta$ has been calculated to be $\sim$80 μm by Hayashi et al. [4], with $\varepsilon' = \sim$40, $\mu' = \sim$1.7, and $\sigma = \sim$1.0 × 10$^2$ (S/cm). According to Eq. (2), an increase in the electrical conductivity causes a decrease in the penetration depth, whereas an increase in the permittivity has an inverse effect. If the values of both $\sigma$ and $\varepsilon'$ increase to the same extent, the effect of the electrical conductivity would be dominant, causing a decrease in $\delta$. This explanation is in excellent agreement with that provided by Peng et al. [10]; they reported a decrease in the penetration depth of Fe$_3$O$_4$ from 0.0153 to 0.0023 m despite a significant increase in $\varepsilon''$ from 1.0976 to 83.3109 with an increase in the temperature from 24 to 880 °C. The penetration depth of a compacted magnetite sample would be shallower than 80 μm owing to the increases in both the permittivity and electrical conductivity with an increase in the relative density, as reported by other researchers [4,5,7,8,11,12].
Fig. 2: Average time required for the initial temperature increase in samples MT45 and MT75.

At the initial stages of temperature increase, the dielectric loss could be neglected because of the very low permittivity of magnetite ($\varepsilon'' \approx 0$) [11]. Moreover, Hotta et al. [8] reported an increase in the permeability of Fe$_3$O$_4$ with an increase in the relative density. An increase in the permeability leads to a decrease in $\delta$; moreover, an increase in the electrical conductivity also causes a decrease in the penetration depth (Eq. (2)). Therefore, an early onset of temperature increase in sample MP45 compared to the onset of temperature increase in sample MT45 could be related to the shallower penetration depth of the latter even at low temperatures.

4. Conclusions

To expand our understanding of the interaction between the microwaves and magnetite particles temperatures lower than the Curie point, the effect of the apparent density and particle size of Fe$_3$O$_4$ on their microwave absorption was studied using a microwave generator at 2.45 GHz at 1050 W. The results can be summarized as follows:

1. A lower apparent density leads to a shorter time required for the initial temperature increase owing to higher microwave absorption caused by the higher electrical resistivity of the material.

2. At temperatures lower than the Curie point, the particle size of Fe$_3$O$_4$ has no effect on the time required for the initial temperature increase in the presence of the H-field. In the maximum E-field mode, Joule loss is the dominant mechanism for heating, leading to a higher temperature in a sample with larger particles, because of their higher electrical conductivity.

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