Microwave Frequency Effect for Reduction of Magnetite

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In this paper, pig iron production by microwave heating is experimentally investigated. In order to explore possible effects of the microwave frequency, identical mixtures of magnetite and carbon powder were processed in different microwave systems operating at 2.45 GHz and 30 GHz, respectively. The weight ratio of magnetite and carbon in the powder mixture was 89:11 weight%. According to the corresponding chemical equation, this should allow to produce pig iron that includes 2 weight% of carbon. High-quality pig iron was obtained in the 30 GHz heating system *in air*. At 2.45 GHz heating *in nitrogen gas*, pig iron was obtained. However, under similar conditions of 30 GHz heating system *in air*, FeO was mainly obtained. This result suggests that the chemical reduction of magnetite is more efficient at higher microwave frequencies.

Keywords: microwave processing, millimeter-wave processing, magnetite, pig iron

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1. Introduction

Microwave technology is not only a substitute for conventional heating, but it resides in the new domain of materials science, including microscopic and strong thermal non-equilibrium systems [1]. In addition, the volumetric heating by microwave during metal powder sintering was reported [2]. The application of microwaves in the iron industry may be characterized by a high potential for an essential reduction of carbon dioxide emission. Iron-ore refinement using blast furnaces was realized with the same basic furnace structure based on the same principle for two centuries. We have conducted a series of experiments to prove the effectiveness of rapid and high-purity refinement under low temperature and oxygen-containing environment using microwave applications, and achieved very positive results.

Nagata and coworkers of the Tokyo Institute of Technology have been working on the development of a unique ultra-high-purity iron refinement technology based on an ancient Japanese iron refinement method called “Tatara” [3]. Their findings on microwave sintering of powder metals led to the idea that rapid refinement of iron is possible by application of 2.45 GHz microwaves, instead of relying on carbon fuels for heat production. Joint experiments at the National Institute on Fusion Science (NIFS) and Forschungszentrum Karlsruhe (FZK) proved that iron with a low carbon concentration of about 1% could be produced. Experiments performed at 2.45 GHz in Nitrogen atmosphere with natural iron-ores demonstrated that high-purity pig iron can be produced with less than 1/10 of impurities compared with iron produced using modern blast furnaces [4, 5]. Moreover, such a microwave process can reduce the carbon consumption to 2/3. Essential prerequisites for reaching the target of reduced CO_2 emission and for satisfying the requirements of steel industry with respect to production capacity are the availability of powerful microwave sources and sufficient supply of electric power, which is not obtained using fossil energy. The most powerful microwave sources currently available are the so-called gyrotrons that can produce power up to 1 MW, when in continuous operation. They were recently designed and developed for plasma heating in fusion experiments [6]. Therefore, feasibility studies were conducted using a compact 30-GHz gyrotron system at the Forschungszentrum Karlsruhe. These studies investigate the potential effects of microwave frequency. Therefore, samples of magnetite powder mixed with carbon powder were processed in different microwave systems. In the following, we discuss the recent experimental results obtained by 30-GHz millimeter-wave (mm-wave) processing *in air*, and processing in a 2.45 GHz centimeter-wave (cm-wave) microwave system *in air* and *nitrogen gas*.

2. Experimental Procedure

2.1 Setup of the mm-wave Process

For mm-wave experiments, the applicator of a compact 30-GHz gyrotron system was used, as shown in

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Fig. 1(a) [7]. The mm-wave power generated can be controlled from 0-15 kW in continuous wave operation using a gyrotron oscillator. This power is launched via a quasi-optical transmission line through a vacuum-sealed boron nitride window into the hexagonal applicator, which is characterized by improved field homogeneity.

The samples used were mixed powders of magnetite and carbon. The grain size of the magnetite with a purity of 99% was less than 1 micrometer. The grain size of the carbon powder used was less than 5 micrometer, and its purity was 99.7%. The weight ratio of magnetite and carbon in the powder mixture was 89:11. According to the corresponding chemical equation, this should allow to produce pig iron, which includes 2 weight% of carbon. About 80 g of such powder sample was filled into an alumina crucible surrounded by thermal insulation (see Fig. 1(b)). The temperature was measured using two S-type thermocouples, one placed at the center of the powder sample, and the other near the crucible wall. The heating process was controlled according to a preset temperature–time program with a heating rate of 70°C/min using the temperature signal of the thermocouple placed near the sample surface.

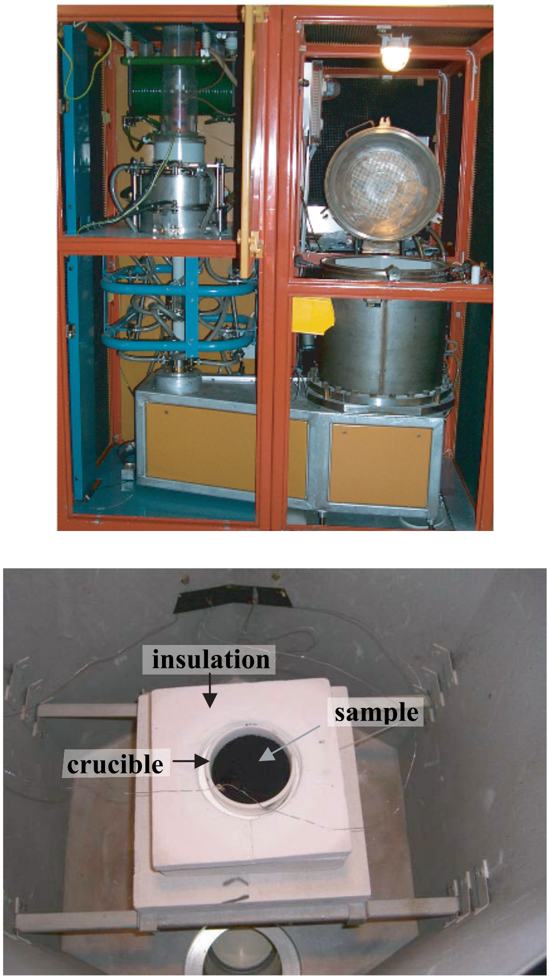

Fig. 1 (a) 30GHz gyrotron system (top),
(b) Experimental setup of the mm-wave (bottom).

2.2 Setup for cm-wave Process

The multimode test furnace at the National institute for Fusion Science, as shown in Fig. 4, was employed for the present study. According to the concepts developed in Germany, to improve the homogeneity of the electromagnetic field, the applicator shape must be hexagonal [8]. The furnace with a volume of 0.92 m^3 is equipped with five magnetrons. The magnetrons generate 2.5 kW, each at 2.455 ± 0.030 GHz. Each magnetron has small differences in frequency and the beat of waves occurring in the chamber. In addition, two mode stirrers scatter the stand-

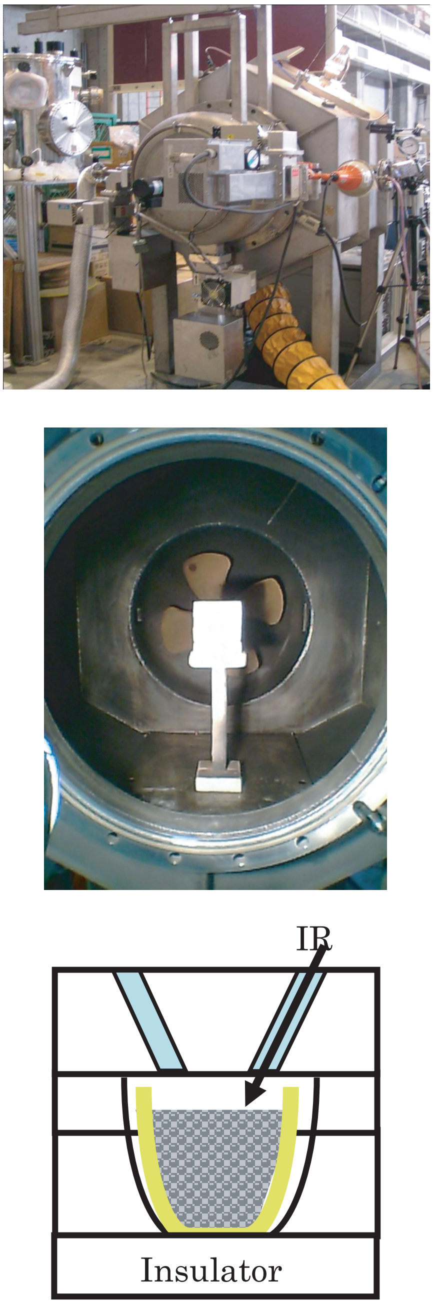

Fig. 2 (a) 2.45GHz magnetron system (top),
(b) Experimental setup of cm-wave process (middle),
(c) Sketch of experimental setup (bottom).

ing wave, easing the non-uniformity due to the standing mode in the chamber. The powder samples used had the same weight ratio of magnetite and carbon power as for the mm-wave process. The powder samples were filled into an alumina crucible surrounded by thermal insulation (see Fig. 2), similar to the setup used for the mm-wave process. The temperature was measured by an IR pyrometer. The heating process was controlled according to a preset temperature–time program with a heating rate of 70°C/min using the temperature signal measured at the top of the sample surface using an IR pyrometer. In addition, a multipoint emission spectrometer examined the sample surface through a special window in the microwave furnace.

3. Results and Discussion

Figure 3 shows the temperatures measured during mm-wave heating of an 80-g powder mixture of magnetite and carbon *in air*. During initial heating, i.e., during the first 15 min, the temperature measured at the sample surface was higher than the temperature measured within the sample volume, indicating limited penetration of the microwave into the powder sample. However, at about 1100°C, the absorption behavior of the powder is changed drastically. According to the iron-carbon phase diagram, this temperature is close to the point, where iron with 2% carbon content liquefies, suggesting that the microwave energy is consumed by the melting process and heating of the material stagnates. Due to this melting, a strong rearrangement of the processed material occurs, leading to changes in the thermocouple positions as well. Finally, when the material is completely molten, the thermal conductivity of the material increases. Thus, the measured temperatures converge to each other. Figure 4 shows the obtained pure pig iron, which was analyzed using an energy-dispersive X-ray spectrometer (EDX). EDX analysis along the cross section revealed a carbon content of about 1 weight%. No oxygen was detected.

Figure 5 shows the process temperatures recorded during heating of a more-or-less identical sample set-up *in air*. However, in this case, heating was performed using the cm-wave system. After 15 min from the start at about 900°C, strong radiation appeared due the ignition of plasma at the sample surface; however, at 1000°C, strong radiation was not observed. In addition, at a temperature of about 1300°C, the absorption behavior of the powder changed, probably indicating the beginning of the melting

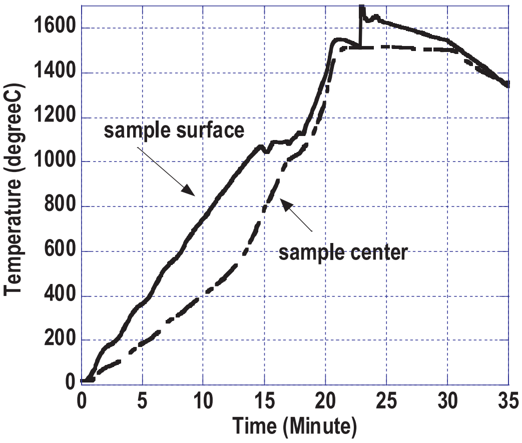

Fig. 3 Measured temperatures during the mm-wave process.

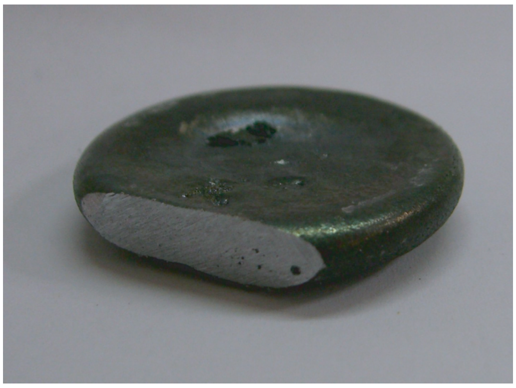

Fig. 4 Pig iron from the 30 GHz mm-waves process.

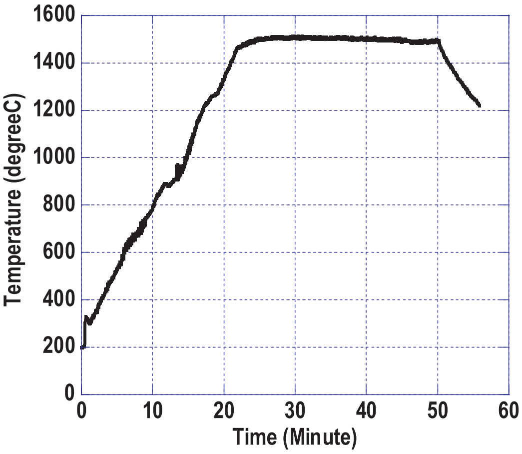

Fig. 5 Measured temperatures during the cm-wave process.

Fig. 6 Sample after 2.45 GHz processing.

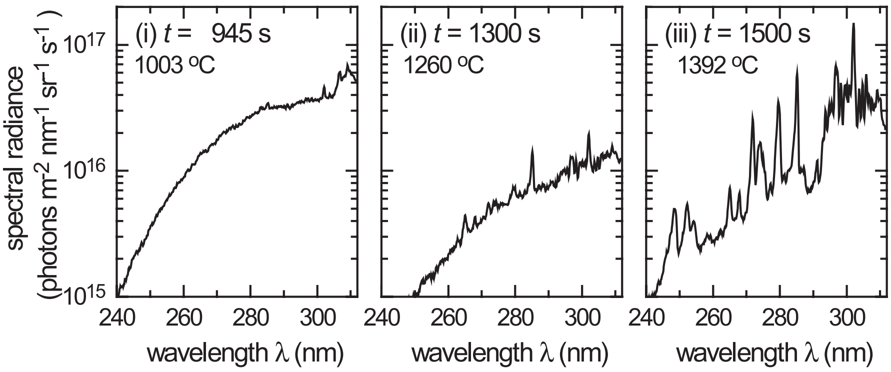

Fig. 7 Evolution of the emission spectrum. Continuous spectrum incl. OH lines around 308 nm (i). Discrete line spectrum showing iron atom lines (iii).

process of iron cores.

Figure 6 shows the material obtained by this process. The sample was analyzed by X-ray Diffraction (XRD). The XRD results revealed that the obtained material mainly consisted FeO after cm-wave heating *in air*.

Matsubara and coworkers measured the time evolution of the emission spectrum during cm-wave processing *in nitrogen gas* using a multi-point emission spectrometer [9]. The spectral intensity of the continuous spectrum is at-least three orders of magnitude larger than that of black body emission for the temperature range of 860-1070°C, measured simultaneously using the pyrometer.

The pattern of the continuous spectrum is somewhat similar to the spectrum radiated by the free-band electron transition. The origin of this continuous emission spectrum is solid-state fluorescence, called cathodoluminescence, induced by impingement of a plasma electron onto the magnetite surface. This results in the excitation of electrons from the valence band into the conduction band, and de-excitation occurs along with a broadband emission, called cathodoluminescence. Cathodoluminescence of magnetite was studied by Balberg I. and J. Pankove [10]. They obtained the emission spectrum of the cathodoluminescence showing an emission edge at 310 nm extending to above 620 nm, with the main peak at about 480 nm and a sub peak at about 390 nm.

With increasing temperature to values higher than 1260°C, the initially observed continuous spectrum is more and more superimposed by a line spectrum, as can be seen in Fig. 7. Most spectral lines can be assigned to electronic excitations of iron atoms, since they were observed in arc and spark discharges [11, 12]. In this stage, the sample surface was seen melting in the video camera image. It can therefore be said that the growth of the discrete line spectrum represents the reduction process of magnetite.

4. Conclusions

High-quality pig iron could be obtained from powder samples of mixed magnetite and carbon by 30-GHz mm-waves heating *in air*. However, in case of heating by 2.45 GHz cm-wave, FeO was mainly obtained under similar conditions *in air*, suggesting that the reduction process could not be completed. Assuming otherwise similar process conditions within the different microwave systems, the results obtained thus far may indicate that there is an influence of the microwave frequency. The one possibility is the effect of cathodoluminescense, because in mm-wave process, the noises of temperature measurement by cathodoluminescense were not observed in signal of thermocouples.

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