Green-Tech Microwave Studies at Tohoku University

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1. Introduction

Microwave heating applications for environmental technologies have been studied since the discovery of microwave heating in 1940's[1]. They were applied for industrial waste treatments, regeneration of active carbon catalysis[2], detoxification of asbestos fibers[3], and recycling of metals[4]. In these applications, the characteristic features of microwave heating are important to be taken into consideration, as a means for rapid, internal and selective heating. This article is intended to introduce some of our recent research topics on microwave applications for environmental technologies. The selected projects deal with the following two subjects:

Diesel Particulate Filter (DPF) - Rapid heating by microwave irradiation (Project A)

The use of diesel engine has been revived recently, because of its high thermal efficiency, less CO_2 emission, and the possibility to scale up to the large driving capacity. However, it emits particulate matter (PM), which is harmful to human bodies[5]. Therefore, PM is captured from the exhaust gas with a DPF before emission to the ambient atmosphere[6]. Currently, the PM choked by the DPF is combusted with blowing air and fuels after predetermined periods or mirages. For the small PM filtration such as PM2.5, fine meshed filter is required, however, it leads to much easier choking. Therefore, instantaneous PM combustion, especially upon ignition (cold start phase) is demanded. Microwave rapid heating has been taken into consideration. In this study, we attempted to fabricate DPF material for the microwave rapid heating.

Vapor de-phosphorization from Tri-calcium phosphate (Project B)

Phosphorus is a valuable element which is essential for human body, growing plants and indispensable as a raw material for various industrial chemical products[7]. On the other hand, phosphorous natural resource is running short, recently. Therefore, it is required to recycle the phosphorous from used materials or waste. Large amount of slag is emitted as by-products in ion and steel making industry, which contains large amount of phosphorous in the form of oxides. It is intended to reduce it with carbon.

In this study, carbon reduction by microwave heating thermal process is applied, because it enables to acquire phosphorous in vapor phase. Rapid vapor removal from the heated body is esential[8], because the slag usually contains ion oxides, which is also reduced to (liquid) metal iron and absorbs phosphorous. This paper reports on the carbon reduction kinetics of slag related materials (TCP: TriCalcium Phosphate, $3CaO{\cdot}P_2O_5$ with and without iron oxides), as a fundamental research study on the phosphorous recycling process.

2. Materials and Methods

In Project A, glass (SiO_2 – RO, R: alkaline earth metal) and stainless steel (SUS303) powder mixture was sintered at 950°C for 1 hour. Porous cylindrical metal/glass compacts (of 15-mm diameter, 5-mm length) were obtained for DPF. In this process, an aqueous slurry of powder mixture was infiltrated into polyurethane sponge preform, then it was fired to burn out the preform. Porosity was determined by Hg porosimeter. They were placed at a position of maximum magnetic field in a single mode microwave applicator operating at 2.45-GHz. Carbon black powder (PM simulants) was contained in the DPF in advance, as a simulating PM. Their combustion kinetics were examined by measuring the CO/CO_2 concentration in the flowing gas.

In Project B, powder mixtures of graphite and TCP, with and/or without ion oxide (Fe_3O_4) were contained in a silica cell tube of a 10-mm diameter

(~25-mm tapped height). Single Fe_3O_4 reduction kinetics was also studied. They were also heated at maximum magnetic field in a single mode 2.45-GHz microwave applicator. The degree of carbon reduction of single TCP was determined measuring the phosphorous concentration by ICP (Inductively Coupled Plasma) analysis of the residue (phosphorous containing calcium oxide). On the other hand, however, the reduction ratio of TCP with iron oxide mixture was difficult to evaluate, because of the problem in separating small iron particles (hence phosphorous concentration distribution in the reduced iron and TCP was not accomplished).

3. Result and Discussion

Microwave DPF heating (Project A)

An example of the obtained DPF is shown in Fig. 1(a), having porosity of 60~70%. The pore size has a range of several nanometers to several hundred micron meters. Stainless steel particles (white color particles) are distributed in the glass matrix (gray color area) as shown in Fig. 1(b). An example of heating curves is demonstrated in Fig. 2 for the cases of 400-W input power[9]. An increase of the metal volume fraction leads to a faster heating rate, thus the time to reach a temperature of 600°C (the PM combustion temperature) becomes shorter. However, as indicated in the Fig.2, a tendency of unstable heating occurs in the case of 40% by volume (40vol%) at 60 s, due to local arcing. Therefore, we have selected the optimal metal fraction as 30vol%, and continued further tests.

The time variation of the exhaust gas composition was detected, as plotted in Fig. 3. CO and CO_2 gases by PM combustion were detected after about 25 seconds of microwave heating. Combustion of carbon black was confirmed to occur under the air flowing condition (500 ml/min) in the laboratory scale experimental system. In the present study, over 10 seconds were required to reach 600°C for PM combustion.

For DPF material having rapid heating capability, it was decided to use a metal/glass composite body for the following reasons: (a) The metal particle has a rapid response to microwave irradiation, hence it is rapidly heated by an induction heating mechanism. The volumetric rapid heating of DPF body can be accomplished by rapid heating of metal particles embedded in non-absorbing matrix, such as a glass, through which the microwave penetrates to the interior.

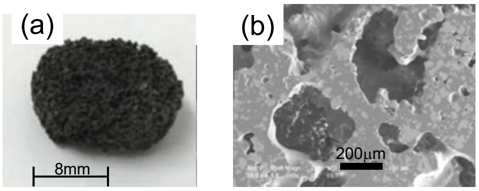

Figure 1. (a) The fabricated DPF, and (b) its microstructure observed with SEM. The volume fraction of stainless steel particles is 30%.

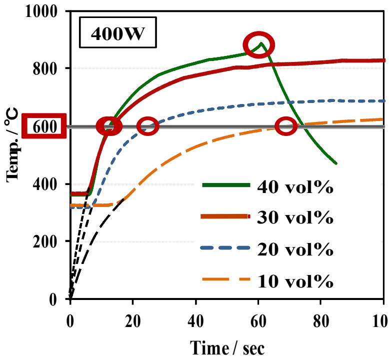

Figure 2. Heating curves of DPF having various metal volume fractions at 400-W power input[9].

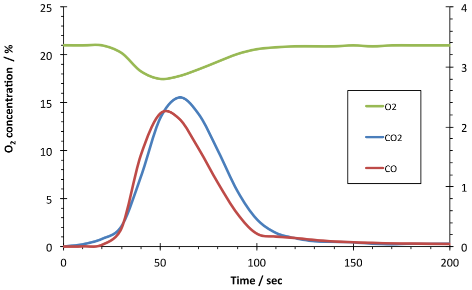

Figure 3. Temporal variations of the exhaust gas composition from DPF.

Otherwise, microwave absorbing ceramics are the other candidates. In Practice, SiC has been taken into consideration for DFP. Currently, microwave heating has not been adopted in practice, though the possibility of microwave heating of SiC-DPF was reported[10]. However, it still takes a longer heating time than our present cases. In our study, it is still required that the heating time has to be shortened by modifying the DPF microstructure, and by developing the materials by considering the durability against the cyclic heating of the composite body.

De-phosphorization by microwave heating (Project B)

The chemical reaction of reduction is given by:

$$\begin{aligned}&3CaO\cdot P_2O_5(s)+5C(s)=\\&\quad P_2(g)+3CaO(s)+5CO(g)\end{aligned} \tag{1}$$

The predicted equilibrium phase constitution (thermodynamic analysis by HSC Chemistry, Ver. 7.0) is illustrated in Fig. 4. The reduction of TCP occurs, and P_2 and CO gas generation is expected to occur, above 1300ºC. As the temperature increases, the partial pressure of these gases becomes higher. The reduction experiments by microwave heating were conducted for the specimen powder mixtures contained in a silica cell, placed in a silica tube of 40 mm in diameter. The vaporized phosphorous was deposited on the inner surface of the silica tube, as shown in Fig. 5. The yellow-brown colored deposits were chemically analyzed and confirmed to be phosphorous.

The reduction ratio of TCP is presented in Fig. 6 at various heating rates and target temperatures. It is shown that the lower heating rate and the higher target temperature resulted in the larger reduction ratio. This is as expected, because of the principle that the total residence time at high temperature causes the higher degree of reduction reaction. Therefore, the reduction ratio was calculated under the assumption of the additive law (the heating process is discretized by steps k (k=1,2,3…n) with increments of time and temperature, Δt and ΔT, respectively, as follows:

$$\alpha_n=\sum_{k=1}^{n}\left[A\exp\left(-\frac{E}{RT_{k-1}}\right)\right](1-\alpha_{k-1})^m\,\Delta t\ , \tag{2}$$

where A is a constant, R is the gas constant, and E is an apparent activation energy of the reaction (E = 220 kJ/mol for the reaction in Eq. 1) [11]. In this equation, the reaction rate constant is expressed in an exponential form of temperature dependence. The calculated reduction ratio (α) is also presented in Fig. 6 by solid lines. In this study, the reaction order index m was best fitted to be 3. The drawn lines in Fig. 6 were obtained under this assumption of reaction kinetics.

It is shown that the reduction occurs at 1100ºC, a temperature lower than estimated by the thermodynamic calculation presented in Fig. 4. One of the possible reasons is that the surface temperature recorded by the optical method was lower than expected. However, we obtained the apparent third order (m = 3) reaction kinetics by calculation, which is not generally common. What is needed is to consider some other special effects in microwave heating on the reaction mechanism.

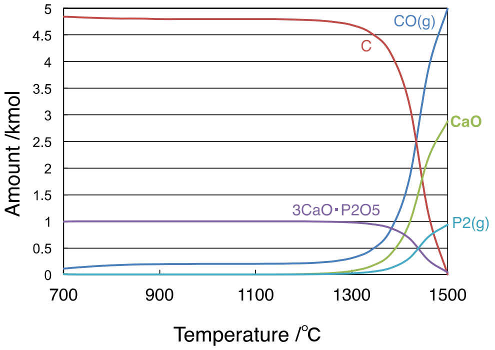

Figure 4. Calculated phase constitution at elevated temperature.

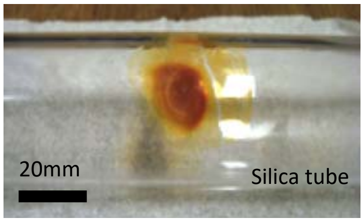

Figure 5. Photograph of phosphorous deposits on silica tube.

The slower heating rate to higher target temperature is favorable for the higher reduction ratio of TCP. However, reduction of Fe_3O_4 occurs much easier as shown in Fig. 7, and mostly reduced above 97% by the range of temperature and heating rates shown in the plot. This fact suggests that the iron oxide is readily reduced to molten metal iron (above 1200ºC, considering the carbon content present). Phosphorous vapor is much easier to be absorbed in molten iron than its solid form.

Considering the results shown in Fig. 6, the degree of reduction becomes large above 1200ºC. Therefore, the operating temperature shall be set above it. The phosphorous has to be vaporized out by rapid heating to 1200ºC before it is absorbed in the molten iron. This requirement is important for the phosphorous recycling process.

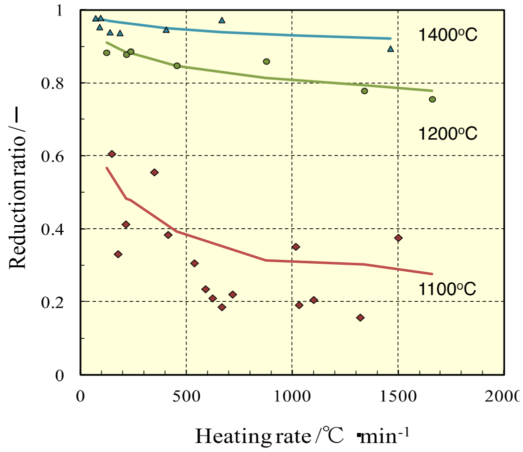

Figure 6. Dependence of experimental reduction ratio of TCP on heating rate for three target temperatures (1100, 1200 and 1400°C); the calculated data are shown by lines.

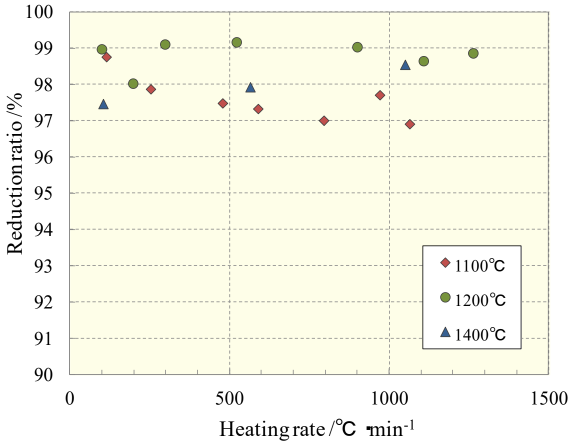

Figure 7. Dependence of experimental reduction ratio of Fe_3O_4 on the heating rate and target temperature (1100, 1200 and 1400°C).

Selected research projects of Green-Tech microwave studies in the authors' group are briefly introduced. First is the fabrication of DPF materials, consisting of metal particle dispersed in glass, which can be rapidly heated, over 10 s to 600°C. Combustion tests of PM simulants were demonstrated. Second, for the purpose of phosphorous recycling, microwave excited carbon reduction kinetics of TCP was studied with and/or without Fe_3O_4. Criterion of heating rate was discussed for phosphorous removal in vapor phase, without being absorbed in the reduced molten iron.

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About the Corresponding Author

Dr. Noboru Yoshikawa has started research work in various fields of materials science and materials processing since his graduation from the department of Materials Science of Engineering (MSE) at Tohoku Univeristy (BSc, MSc and PhD). He is now an associate professor at Graduate School of Environmental Studies at Tohoku Univeristy (combined with the MSE department). He has been in the field of microwave engineering for about twenty years. His main interests is microwave application for materials processing and green technology. He has been involved in many projects and performed many collaborative researches. Currently, he is an administrative member of JEMEA (Japan Society of ElectroMagnetic Energy Application) and JSPS No. 188 University-Industry Cooperative Research Committee.

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