§25. Construction of the Synthesis of Reduced Transition Metal Oxides - CO<sub>2</sub> Decomposition Cycle by Microwave Irradiation

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In this study, the authors try to establish a technology for reducing carbon dioxide (CO<sub>2</sub>) to carbon using a partially reduced transition metal oxide. Since the Industrial Revolution, global emissions of carbon dioxide has increased. In 2050, the world's population will be more than 100 million people and it is predicted that  $CO_2$ emissions will reach 45 billion tons (1.5 times that of 2010) <sup>1)</sup>. To decrease the  $CO_2$  emissions from the industrial, transportation and home field due to the population explosion, it has been made attempts to use CO<sub>2</sub> by decomposing it to carbon. One of the expected method to decompose  $CO_2$  is a contact method that partially reduced magnetite or magnesium metal is contacted with CO<sub>2</sub>. However, the method has a problem that hydrogen (derived from fossil fuels) reduction treatment is need to reduce magnetite or magnesia.

To obtain the partially reduced transition metal oxides required for decomposition of  $CO_2$ , the authors focus on the microwave reduction method. We plan to use the microwaves which obtained from electrical power generated by nuclear fusion and reform  $CO_2$ . To progress this research, it is necessary to pursue a scientific principle of  $CO_2$  decomposition by microwave through in-situ measurement during microwave irradiation. In this report, as an initial experiment, we irradiate microwaves to magnetite for reducing it. While microwave irradiation,  $CO_2$  gas flowed and contacted with magnetite, and the  $CO_2$  reduction behavior at each temperature was investigate by using gas chromatography.

Magnetite powder (1  $\mu$ m under, Kojundo Chem., Lab. Co., Ltd., Saitama, Japan) was used as a starting materials. The powder was filled into a test tube. The powder was hold by silica wool at upper and bottom of powder. The test tube was set at the maximum point of a microwave magnetic field in a single-mode cavity (Fig. 1). Flowing gas is composed of nitrogen (base gas) and CO<sub>2</sub> and a flowing rate was controlled by a mass flow controller. After the sample temperature reached to a predetermined temperature, gas was started flowing and gas troughed in the powder was analyzed by the gas chromatography.

Figure 2shows a photograph of the sample during microwave irradiation. Before microwave irradiation, the test tube was filled with sample powder. From Fig. 2, samples powder was sintered at high temperatures and the volume became small. Therefore, efficiency of  $CO_2$  decomposition became poor since the reduction reaction area (surface of magnetite powder) of  $CO_2$  was reduced by

sintering. It is difficult to analysis of decomposition rate because the surface area can't be calculated precisely. We will have to improve a sample setting. XRD results of the weak-sintered sample showed that the phase of it was same as the starting material. However, peaks of the sample after heating were shifted to lower angle side and it is suggested that magnetite was oxidized. In addition, the sample temperature was not uniform and the powder at upper area was oxidized and the powder became hematite. From analysis of gas chromatography, carbon monoxide (CO) which derived from CO<sub>2</sub> reduced by magnetite was detected. The amount of CO gas was increased with the temperature of the sample increasing. From the temperature dependence of CO concentration in flowing gas, reduction reaction of  $CO_2$  was reproduced in the conditions. These results suggest that the reduction reaction of CO<sub>2</sub> was definitely occurred and it is highly probable that the partially-reduced magnetite reduced CO<sub>2</sub>.

Although 1400 °C need to reduce magnetite effectively, we could not achieve the temperature. One of reason is the sample was powder and the microwave absorb rate was poor. Another reason is the sample was cooled by nitrogen and  $CO_2$  gas. The rise of the sample temperature is one of the major challenges to construct the cycle of the synthesis of reduced transition metal oxides -  $CO_2$  decomposition.



Fig. 1. Schematic view of the experimental system



Fig. 2. Photograph of the sample during microwave irradiation

1) European commission: *World Energy Technology Outlook-WETO-H*<sub>2</sub>.