§21. Reduction Reaction of Ferromagnetic Oxides under Microwave Irradiation

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Microwave is applied to heat materials, water, food and plasma. Microwave oven is developed in 1960s and microwave heating is familiar with our life, however, mechanism of "Microwave heating" is under discussion. Especially, from 1990s, the phenomenon, which cannot be explained by thermodynamics, was reported and researchers have investigated the phenomena to understand the mechanism of it. Microwave energy has been attention to synthesize novel materials. We have to understand the interaction between electromagnetic wave of which has GHz frequency and materials for maximizing the microwave effect. The special effects of microwave only occur during inducing the microwave energy to materials. The energy flow is key to understanding the microwave effect. The non-equilibrium reaction is the discipline between materials science, which are based on equilibrium thermodynamics and plasma science, which is based on nonequilibrium dynamics. In the study, the authors investigate a reduction behavior of ferromagnetic materials during microwave irradiation and reveal the interaction between electromagnetic wave and materials using plasma physics (dynamics).

Experiment was conducted using the device to measure mass of gas emitted from a sample during microwave irradiation. The details of the device have been reported[1]. Nickel manganate ($NiMn_2O_4$) was irradiated with microwave at the maximum point of H-field or electric furnace. Before in-situ gas analysis experiment, a pellet sample of $NiMn_2O_4$ was synthesized by electro furnace from mixed powder of NiO (99.9 % up, Kojundo Chem. Lab. Co. Ltd.) and $MnCO_3$ (99.0+ %, Wako Pure Chem. Inc. Ltd.) at 850 °C for 12 h. The synthesis procedure was repeated three times and the authors obtained single-phase $NiMn_2O_4$. The sample was re-grounded and pelletized to ϕ 8 mm. The sample was irradiated with microwave using single-mode TE_{103} cavity in vacuum. In the experiment, a semiconductor oscillator (Nagano Japan Radio Co., Ltd., NJZ-2450) was used. For comparison, another sample was heated in an electric furnace.

Figure 1 shows the partial pressure of oxygen during conventional heating using electric furnace. Oxygen was emitted gradually from about 300 °C, and over 300 °C, partial pressure of oxygen increased constantly to 500 °C. Then, although partial pressure of oxygen decreased to about 5 x 10^{-4} Pa, it increased again from 570 °C. At 660 °C, partial pressures of oxygen were dropped and then increased slightly. Figure 2 shows the partial pressure of oxygen during conventional microwave H-field irradiation. Oxygen was emitted rapidly from 200 °C to 260 °C, and then, around 300 °C, it was dropped and then increased gradually to 3 x 10^{-2} Pa. These results mean that oxygen emission in microwave irradiation occurred at lower temperature in comparison with conventional heating.

Microwave effect of the chemical reaction has been discussed using transition state theories[2]. From the Arrhenius plots, the activation energy in conventional heating and in microwave irradiation was obtained. Substituting the experimental values such as microwave Q value, $m^* \xi^2$, which indicates the perturbation of materials by microwave E-fields, is estimated. On the other hand, $m^* \xi^2$ is obtained by the results of the experiment. The $m^* \xi^2$ value is about fifty times larger than the former-estimated $m^* \xi^2$ value. The difference resulted from that the theoretical study is based on the perturbation induced only by microwave E-field. Thus, the results indicate that further theoretical study required explaining the chemical reaction in microwave H-field irradiation.

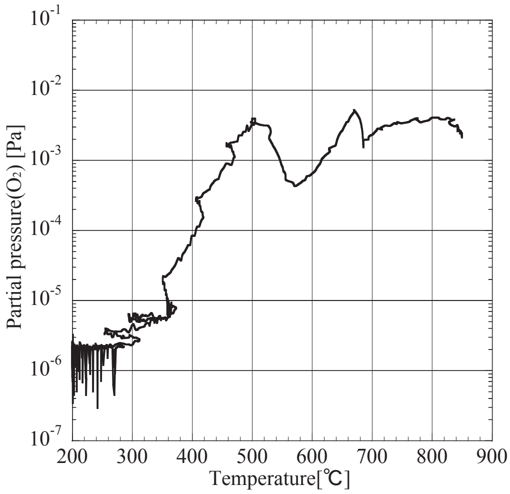

Fig. 1. Partial pressure of oxygen during conventional heating of $NiMn_2O_4$

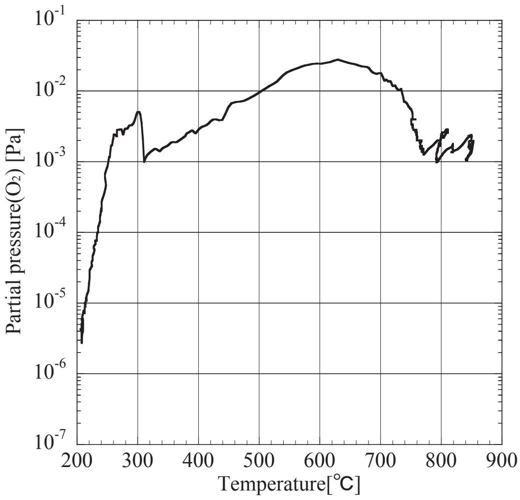

Fig. 2. Partial pressure of oxygen during microwave irradiation of $NiMn_2O_4$

1) Fukushima, J. et al.: *NIFS Ann. Rep.,* (2009) 420.
2) Sato, M. et al.: *Ceram. Trans.,* **249** (2014) 313-320.