1. Introduction

Microwave heating has become a new form of supplying energy, instead of heating with fire. It is well known that a metal powder can be heated in microwave field and reaches high temperature quickly. According to basic electromagnetic theory, we can calculate the heating rate from the permittivity and permeability. Until a few years ago, cautious treatments were required to calculate the rate because these data for metal powder at microwave frequency were insufficient. Recently, many data were reported and the mechanism has been studied extensively to apply several industrial processes.1,2) The mechanism of the heating became clearer little by little.

Chemical reaction caused by microwave field goes noticed as the heating mechanism has been studied. It was reported that a reduction with microwave heating shows different scientific behaviors from that by conventional ones. For example, Ishizaki et al. reported that a reduction of an iron ore started in the microwave field at 200°C lower temperatures than that calculated by thermodynamics.3) It was reported that non-equilibrium state brought the reduction out at low temperature by the selective heating of the microwave.4,5) Authors agree with the fact that microwave heating is selective. But the fact does not indicate that extra-thermodynamic reaction is result from the differential heating.

Authors noticed that microwave nitrides metal titanium powders in air as a good example of extra-thermodynamic phenomena. In conventional heating, metal titanium is easy to get oxidized in air and makes its surface oxide film. But microwave can make the metal titanium nitriding in air. This phenomenon is extra-thermodynamic and shows us the best feature of microwave chemistry to author’s knowledge (the phenomena is reported only as patent technology).

In this paper, metal titanium powders were heated by microwave irradiation. An oxygen partial pressure from the heating system is measured to understand the mechanism of the nitriding. Furthermore, the mechanism is discussed from the quantum-chemical view.

2. Measurement

2.1. Single Mode Microwave Furnace System

The experiments were conducted in a single mode waveguide cavity (called a microwave furnace in this paper), which consisted of a WRJ-2 (109.1/11003 56.4/11003 149.3/11003 5 mm) waveguide. One end of the cavity was closed by a movable reflector (plunger) and the other end was coupled with the microwave generator through a slotted plate (iris: a slit of the iris is cut in parallel with an electric field direction and is 28 mm in widths), as shown in Fig. 1.

The test piece was made of titanium powders (TIE06PB, Kojundo Chemical Laboratory Co., Ltd.) and was placed at magnetic max in the cavity. The volume of the piece \( f \times 5 \) mm compacted by 50 kg/cm\(^2\) force) was kept small to prevent disturbing the structure of electromagnetic field of the TE103 mode in the cavity. When the test piece was inserted, the equivalent cavity length was shortened by a few millimeters to maintain the overall dielectric constant.

The temperature of the test piece was measured with optical thermometer (FTZ6-R220-50L22, Japan Sensor Corp.).

2.2. Measurement of an Oxygen Partial Pressure in Exhaust Gas

An oxygen partial pressure in exhaust gas from heating system was measured using an oxygen sensor made of solid electrolyte. During the application of the heating, the pressure decreased to an order of 10\(^{-10}\) atm and quickly increased to an order of 10\(^{-5}\) atm and then oxygen emission peaks were observed. Furthermore, the nitriding mechanism was discussed for Ti\(_3\)O\(_5\) model in terms of quantum chemistry. The quantum-chemical simulation showed that Ti–O bonding of titanium oxide is anti-bonding and consists of 3d orbital. The orbital becomes steady state by removing an oxygen atom from the model.

KEY WORDS: microwave heating; metal titanium powder; oxygen partial pressure; 3d orbital; titanium oxide; nitriding mechanism.
(99.99) gas was flowed into the pipe from the microwave furnace at a rate of 200 mL/min, as shown in Fig. 2. The cell equation is described as

\[ \text{PtO}_2(P'_O) | \text{ZrO}_2 | \text{O}_2(P''_O), \text{Pt} \]

Where, the reference electrode was air \((P'_O = 0.21 \text{ atm})\). The oxygen partial pressure of the output gas was calculated from the temperature and voltage of the chamber. A sensor needs high temperature to work exactly. It was measured that the temperature of the sensor decreased after N₂ gas was flowed. The sensor was kept over 800°C in an electric furnace.

The metal powders were analyzed by an SEM (Scanning Electron Microprobe, JSM-5600 JEOL) and XRD (X-ray Diffractometer, rint-2200vtk, Rigaku Denki) after the heating.

3. Results

2.45 GHz microwave heating made metal titanium powders gold. Figure 3 shows secondary electron image of titanium powders before microwave heating (a) and after microwave heating (b). Sintered powders were observed as shown in Fig. 3(b). Microwave dropped it’s energy into the metal surface and made the surface melting.

The result of XRD (X-Ray Diffraction) indicates that the microwave heating nitrides titanium powders at high oxygen potential (an order of \(10^{-40}\) atm partial pressure) despite titanium makes it’s surface titanium oxide easily. By conventional heating, the oxidation of titanium metal occurs at very low oxygen potential (an order of \(10^{-40}\) atm at 627°C). It is noticeable that peaks of a titanium nitride were observed after microwave treatment in air as shown in Fig. 4. This phenomenon against thermodynamics is well known and was observed in our system.

An oxygen partial pressure in the N₂ carrier gas was \(2 \times 10^{-5}\) atm. When the microwave was irradiated to titanium powders, the pressure decreased to an order of \(10^{-10}\) atm and quickly increased to an order of \(10^{-5}\) atm as shown in Fig. 5. It is noticeable that pulse signals of oxygen rising were observed. In this region, the oxygen potential suddenly increased over the potential of supply gas. Microwave field changes Ti powder’s temperature 1 000°C and the oxygen potential decreased to the order of \(10^{-10}\) atm in this region. Then, the temperature decreased under 400°C and gradually increased to 800°C. The temperature kept stable state and pulse signals were observed in the region. It is noticeable that these signals were also observed to heat metal nickel powders at magnetic max point.

4. Discussion

4.1. Mechanism of Microwave Heating for Metal Titanium and Energy Path

The discussion will be focused on the macroscopic mechanism of the nitriding. When the microwave was irradiated to titanium powders, the oxygen partial pressure de-
creased and then increased to the value of the flow gas. The decreasing of the pressure means the oxidation of the titanium powder. Kimura et al. reported that a reaction product includes a titanium oxide in 28 GHz microwave heating. The oxidation was ruled by the oxygen transportation because the titanium oxygen was observed in the tapped sample. The metal titanium got oxidized and then became titanium nitride in microwave field because microwave reduces TiO$_2$/H$_2$O$_x$ to metal Titanium at high oxygen potential.

What mechanism does reduce TiO$_2$/H$_2$O$_x$? Authors notice the difference of the energy path from conventional heating. Tanaka et al. reported selective heating mechanism of magnetic titanium oxides. In microwave field, electron spins face in the same direction and the state vanished at the Curie point. Energy saved by electron spins makes the temperature of the titanium oxide over the Curie point. The result of Fig. 5 agreed with the theory and has validity. Electrons which receive the microwave energy are in 3d orbital of titanium oxide because Heisenberg model described the heating behavior well. The orbital is energy path between microwave and titanium oxide.

### 4.2. Thermodynamics and Quantum-Chemical Approach to Clarify Nitriding Mechanism

Microwave heating nitrides metal titanium powders at high oxygen partial pressure ($P_{O_2}$ = 10$^{-7}$ atm). The equivalent vapor pressure of oxygen is about an order of 10$^{-25}$ atm at 827°C. When metal titanium gets heated, oxygen partial pressure should be to the value. At the first of microwave heating, the oxygen partial pressure in the exhaust gas decreased with the time as described before. In the region, oxygen atoms were trapped by metal titanium.

The discussion will be focused on oxygen emission peaks. These peaks were observed after the surface of the metal got oxidized. At first, authors thought of these peaks as a chemical oscillation resulted from non-equilibrium state. If the reaction is the chemical oscillation, the oxygen partial pressure could be described by the thermodynamics. The reaction formulas were assumed to be as following.

$$2Ti + O_2 \xrightarrow{K_1} 2TiO \quad \text{(2)}$$
$$2TiO + O_2 \xrightarrow{K_2} 2TiO_2 \quad \text{(3)}$$
$$N_2 + 2TiO \xrightarrow{K_3} 2TiN + O_2 \quad \text{(4)}$$
$$N_2 + 2TiO_2 \xrightarrow{K_4} 2TiN + 2O_2 \quad \text{(5)}$$

Where, $K_n$: forward reaction rate coefficient for equation $n$, $P_{N_2}$: 0.99999, $P_{O_2}(0)$: 1×10$^{-5}$, [Ti(0)]: 1, [TiO(0)], [TiO$_2$(0)]: 0. In the simulation, activities of each material and partial pressure were function of time. Reaction coefficients were changed from 0 to 10$^4$ and $P_{O_2}(t)$ were calculated for each $K$ combination employing a method of Ref. 9. But there were no $K$ combination which described results of Figs. 3 and 5. Authors tried to describe the result by assumptions of the other formulas and did not succeed in trials. It may be concluded that the other approach was required to account for the nitriding mechanism.

A quantum-chemical approach was employed to clarify the nitriding mechanism. Microwave energy is given to TiO$_2$ via 3d orbital electrons as the evidence that the Heisenberg model accounted for the heating behavior of the system well. The orbital of TiO$_2$ is key point to clarify the nitriding mechanism.

What state is the orbital like? Ti$_{14}$O$_{13}$ cluster model were employed to consider 3d orbital’s roll for the nitriding response as shown in Fig. 6. The lattice constant for TiO is 4.177 Å and the structure is NaCl type. The electron density of states was calculated by DV-Xa method (SCAT code, VESTA). Input data were shown in Table 1. The electron density of states and overlap population diagram for Ti$_{14}$O$_{13}$ model were shown in Fig. 7. Plus value means bonding orbital and minus value does anti-bonding in horizontal axis of the overlap population diagram. 3d orbital of the model is consisted mostly by Ti–O bonding (the overlap population diagram of Ti–Ti bonding is shown for comparison). Wave function for these electrons has large distribution gradient in the bonding and the orbital is less stable.
than 3d orbital of pure metal titanium. It is noticeable that the 3d orbital is positioned near Fermi Level, too. Electrons in the orbital are easy to get microwave energy. Electrons with large distribution gradient are excited by microwave energy, which changes steady state of the system (Ti–N bonding indicates more stable than Ti–O bonding by the simulation). The total electron energy of 3d orbital is corresponding to the electron density of states. If oxygen was removed from the model, the electron density of states of the orbital decreased as shown in Fig. 8. Tanaka et al. reported that the electron spin of the 3d orbital plays an important role in the heating mechanism (Heisenberg model for the spin described the heating behaviors well in the system). The orbital is anti-bonding, which describes the reduction of titanium oxide. The oxygen partial pressure change of this study was accounted for well, too.

5. Conclusion

Metal titanium powders were nitrided by microwave heating at high oxygen partial pressure ($P_{O_2} = 2 \times 10^{-5}$ atm). The potential of the exhaust-gas was measured by solid electrolyte oxygen sensor to understand the mechanism of the nitriding reaction. During application of microwave heating to titanium powders, the pressure decreased to an order of $10^{-2}$ atm and quickly increased to an order of $10^{-2}$ atm and then oxygen emission peaks were observed. Furthermore, the nitriding mechanism was discussed with...
thermodynamic and quantum-chemical approach. As a result, the 3d orbital of titanium oxide consists mostly of Ti–O bonding and is near Fermi Level in Ti$_{14}$O$_{13}$ model. The orbital is anti-bonding and is less stable than the orbital of titanium nitride in microwave field. The orbital is energy path between microwave and TiO$_2$/H$_{11002}$x. It is considered that microwave energy gathers into the anti-bonding of TiO$_2$ and breaks that.

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