doi:10.1246/cl.2012.39

Microwave-energy Distribution for Reduction and Decrystallization of Titanium Oxides

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In this study, we examine the reduction behavior of TiO_{2-x} during microwave irradiation at the maximum point of the H field in a single-mode cavity (H-field irradiation). The reduction of TiO_{2-x} was greater and the decrease in the activation energy (E_a) for reduction was higher when microwave irradiation was used than when conventional heating was used. TiO_{2-x} was decrystallized and formed a nanodomain structure with a 5–10 nm particle size. From these results, we determined the amount of microwave energy distributed as activation, kinetic, and thermal energies.

Microwave energy can transform into not only thermal energy but also chemical and kinetic energy under certain conditions. For instance, in recent studies, we experimentally analyzed the reduction behavior of CuO under microwave irradiation.[1,2] In these studies, we showed that CuO was reduced, not through a thermal reduction process but by the direct transformation of microwave energy into activation energy required for the reduction. As another example, studies by Roy et al. showed that Fe_3O_4 or TiO_{2-x} assumed a noncrystalline form (we call this phenomenon "decrystallization").[3–5] In these studies, the sample was subjected to microwave irradiation at the maximum point of a magnetic field using a single-mode cavity (H-field irradiation). In this paper, we suggest that the microwave H-field energy is transformed into the energy needed for decrystallization because the size of the grains increases at high temperature in ordinary conventional heating. These experimental results suggest that the microwave energy is distributed as thermal, chemical, and kinetic energies at certain rates.

To understand the microwave process, it is necessary to investigate the amount of microwave energy distributed as activation, kinetic, and thermal energies. To quantify the activation energy needed for the reduction of TiO_{2-x}, we need to understand the energy flow that occurs during microwave irradiation. Because the decrystallization of TiO_{2-x} leaves an unpaired electron in the 3d orbital, TiO_{2-x} is useful for studying the microwave-energy distribution.

In this study, we measured the reduction behavior of TiO_{2-x} and compared the activation energy required during conventional heating with that required during H-field irradiation.

We heated a TiO_{2-x} sample in vacuum and measured the quantity of emitted oxygen. Figure 1 shows the experimental system. We used a turbo molecular pump to evacuate the system, which enabled us to measure the changes in the oxygen partial pressure once every second. Rutile powders of TiO_2 (purity: 99.9%, particle diameter: 2 mm, from Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) were used as the sample.

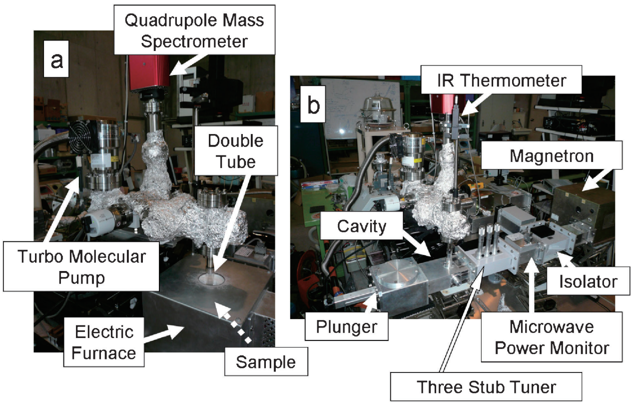

Figure 1. Experimental setup for each type of heating. (a) Conventional heating using an electric furnace and (b) microwave H-field heating using a single-mode cavity.

Before the experiment, the sample was heated in an electric furnace to 900 °C and held at that temperature for 1 h. After preheating, TiO_2 was reduced slightly to form stoichiometric TiO_2 (TiO_{2-x}). The sample was then positioned at the maximum point of the H field using a single-mode cavity (Figure 1b). The TiO_{2-x} sample powder was compacted to $\phi 8 \times 2$ mm, which was sufficiently small to prevent it from disturbing the standing wave in the single-mode cavity. During heating, the microwave input power and the reflection power, sample temperature, total pressure of the system, and mass spectrum of the emitted gas were measured by a digital power monitor, an infrared thermometer, a full-range vacuum gauge, and a quadrupole mass spectrometer, respectively. We used an electric furnace for conventional heating (Figure 1a). Microwave power was increased gradually to 600 W, and the sample temperature was also increased to 1600 °C.

To determine the reduction enhancement, we examine the activation energy required for reduction in terms of the thermal energy. The reduction rate (k) is expressed by the Arrhenius equation. When the logarithm of both sides of the equation is taken, the logarithm of the reduction rate is in proportion to the inverse temperatures. By plotting the logarithm of the reduction rate against the inverse temperatures (called an Arrhenius plot), the activation energy for reduction by thermal energy can be determined.

Figure 2 shows the Arrhenius plot of the reduction rate of TiO_{2-x} with both conventional heating and H-field irradiation. In a previous study, we analyzed the reduction behavior of TiO_{2-x}.[6] However, we could not plot the values obtained as the Arrhenius plot because the sample temperatures used in the previous study were below 1200 °C.

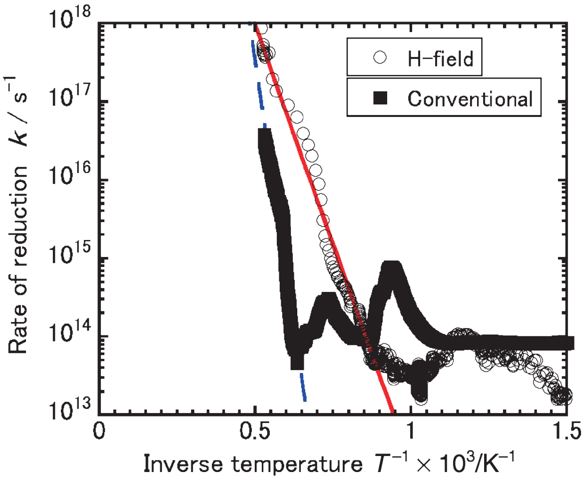

Figure 2. Arrhenius plot of the reduction rate of TiO_{2-x} by conventional heating and by H-field irradiation.

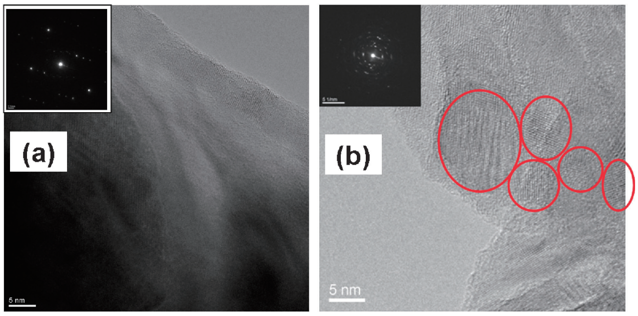

Figure 3. TEM image of TiO_{2-x}. The Laue diffraction image is shown in both TEM images. (a) Conventional heating and (b) H-field irradiation.

In the current experiment, we employed a new electric furnace for heating the sample to 1600 °C, and thus, we were successful in plotting the results as an Arrhenius plot for the conventional heating case. Oxygen was emitted during H-field irradiation at low temperature, unlike during conventional heating, and therefore, the reduction of TiO_{2-x} was enhanced during H-field irradiation. The inclination of the line in the Arrhenius plot indicates the activation energy (E_a). E_a was 517 kJ mol^{-1} for conventional heating and 214 kJ mol^{-1} for H-field irradiation. The difference between the E_a values for the two cases was 303 kJ mol^{-1}. The additional energy (i.e., 303 kJ mol^{-1}) was supplied from the H field directly to the TiO_{2-x} electrons. The average amount of oxygen emitted during H-field irradiation was 1.1×10^{-3} mol. If an activation energy of 303 kJ mol^{-1} was supplied from the H field within 800 s, 12.3 mJ s^{-1} (mW) would be directly transformed by the H-field.

The morphologies of TiO_{2-x} after conventional heating and H-field irradiation are shown in Figure 3. After conventional heating, TiO_{2-x} was crystallized, as the Laue spots were round in shape. On the other hand, after H-field irradiation, the Laue spots appeared as concentric arcs (Figure 3b). This indicated that the crystals became amorphous. However, from the TEM image, it is apparent that TiO_{2-x} was not amorphous. TiO_{2-x} was decrystallized and formed nanodomain crystalline structures with 5–10 nm particle size (the area enclosed in red line in Figure 3b).

The nanodomain formation occurred volumetrically, but the volume of the nanodomain in the sample was less than 20%, as shown in a previous experiment.[7] We assume that the grain boundary was formed by H-field energy. Dawson et al. reported that the calculated boundary energy was 1.72 J m^{-2}, which is quite close to the classical value of 1.70 J m^{-2}.[8] Before H-field irradiation, the sample was in the form of a crystalline powder with a particle size of 2 mm. If the grain boundary was formed gradually within 800 s, 81.6 J s^{-1} would be necessary to form the grain boundary from a single crystal of the raw powder. This value is about 10^3 times greater than the activation energy needed to enhance the reduction. These results suggest that the reduction-enhancement process differs from the structural-change process.

The thermal energy of the heated sample by H-field irradiation was ejected as convection, conduction, and radiation. The total heat value per unit time (Q_t) is expressed as

$$Q_t = Q_g + Q_s + Q_r \tag{1}$$

$$Q_g = \alpha \Lambda S(T - T_0)p \tag{2}$$

$$Q_s = S_a \kappa (T - T_0)/L \tag{3}$$

$$Q_r = S\sigma\varepsilon(T^4 - T_0{}^4) \tag{4}$$

where Q_g is the convection loss, Q_s is the conduction loss, Q_r is the radiation loss, α denotes the accommodation factor, Λ denotes the heat conductivity of free molecules, S denotes the surface area, p denotes the pressure, T_0 denotes the temperatures of atmosphere (300 K), S_a denotes the adjacent surface in contact with the test tube (24 mm^2), κ denotes the heat conductivity of quartz glass,[9] L denotes the characteristic length (the length of the quartz tube: 60 mm), σ denotes the Stefan–Boltzmann constant ($\sigma = 5.67 \times 10^{-8}$ J s^{-1} m^{-2} K^{-4}), and ε denotes the emissivity ($\varepsilon = 0.95$). From the viewpoint of dimensional analysis, Q_g is 100 times smaller than Q_s and Q_r; thus, Q_g is negligibly small. From the sample temperature and the heat conductivity of the quartz glass at each temperature, the average value of Q_s is calculated as 0.8 J s^{-1} (W). The average value of Q_r is calculated as 8.2 J s^{-1} (W). The energy required to increase the temperature of the TiO_2 sample (0.2 g) from 298.16 to 1900 K is 293.5 J;[10] thus, the value is much less than Q_s and Q_r. The transformation of the H-field energy to the thermal energy was mainly used to maintain the sample temperature for Q_s and Q_r.

Figure 4 shows the distribution of microwave energy as the activation, kinetic, and thermal energies. A total of 41% of the input microwave energy was transformed into the activation, kinetic, and thermal energies, and the remainder of the energy (59%) was expended for sintering, cavity loss, etc. The energy distributed as the activation energy was 10^3 times less than the energy distributed as the kinetic and thermal energies. This could be because the reduction was a surface reaction. Oxygen was emitted from the surface of the TiO_{2-x} powders, but the surface area decreased as the sintering of the TiO_{2-x} powders progressed. On the other hand, the formation of nanodomain structure and the temperature increasing are volumetric reactions; thus, the energy required for the formation of nanodomain structure is greater than that required for the reduction.

The distribution of the kinetic energy was about 4.4 times greater than that of the thermal energy. These results are in

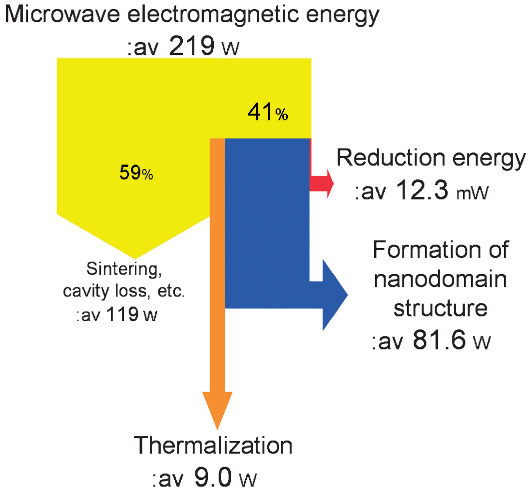

Figure 4. Distribution of microwave energy as the activation energy, which is needed to form the nanodomain structure, and the thermal energy. In the figure, "average" means the average energy within 800 s from the start of microwave irradiation.

agreement with the fact that bigger energy than the energy of grain growth is needed as energy which generates nanodomain structure because grain growth occurs under thermal equilibrium.

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