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Partial reduction of TiO_2 without form transformation using non-thermal plasma

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In this study, we examined the partial reduction of anatase TiO_2, both without form transformation from anatase to rutile and without transformation to Ti_2O_3, using hydrogen plasma. In this experiment, RF discharge plasma (13.56 MHz) was used, and the plasma was generated by a discharge between electrodes attached on the outer surface of a quartz tube. The reduced TiO_2 was analyzed by XRD. Consequently, it was shown that, under the proper conditions, hydrogen plasma can partially reduce anatase TiO_2 at temperatures lower than 800°C, both without form transformation from anatase to rutile and without transformation to Ti_2O_3.

Key words: hydrogen plasma, reduction, titanium dioxide, RF discharge plasma, non-thermal plasma

1. INTRODUCTION

Cold plasma, that is, non-equilibrium plasma, has been used in several industrial fields. In recent years, cold plasma processing has been applied to the reduction of metallic oxides [1, 2]. The reduction of metallic oxides by plasma is often required to prepare a surface of the substrates before treatment [3]..

Titanium dioxide (TiO_2), one of the metallic oxides, is especially attractive as a photocatalyst for heterogeneous catalysis [4-6]. Titanium dioxide crystallizes into three major structures: rutile, anatase and brookite. However, only rutile and anatase play roles in TiO_2 applications, and they have been studied using surface science techniques. Kinetically, anatase is stable, and its transformation into rutile at room temperature is so slow that the transformation practically does not occur. The form transformation from anatase to rutile takes place at $T>600$ ℃ [7]. The reduction of TiO_2 was examined using low-pressure hydrogen-containing plasma in conjunction with microwave plasma [8]. Recently, partial reduction of TiO_2 was performed by the photochemical or electrochemical method [9] and heating [10, 11]

The purpose of the present work was to investigate the partial reduction of anatase TiO_2, both without form transformation from anatase to rutile and without transformation to Ti_2O_3, using hydrogen plasma.

2. Experimental Details

Figure 1 shows the plasma reactor, which is made of a quartz tube set in an electric furnace. The sample of anatase TiO_2 (JA-1, Tayca) particles placed in the quartz boat was introduced into the plasma reactor. In the experiment, RF discharge plasma (13.56 MHz) was used, and the plasma was generated by a discharge between the copper electrodes attached on the outer surface of the quartz tube. The distance between the electrodes was defined as the electrode gap. The electrode gap was 50 mm in Reactor S and 150 mm in Reactor L. The reactor temperature, which was monitored by thermocouples attached to the inside of the furnace, was changed by controlling the electric power of the furnace.

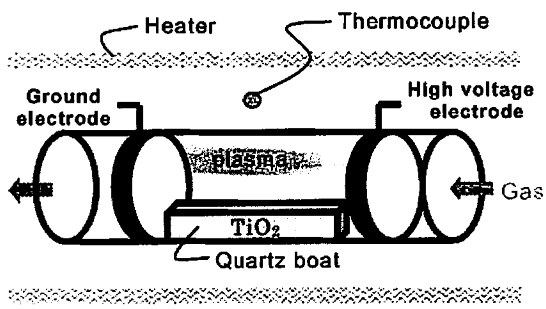

Fig 1. Detailed schematic of the plasma reactor

Before the plasma treatment, the following pre-treatment was carried out to remove the water vapor absorbed by the anatase TiO_2 sample. In the pre-treatment, the flow rate of argon gas was fixed at 40 sccm and the heating temperature was fixed at 500℃, and the treatment time was about 30 min. In the plasma treatment, the flow rates of argon and hydrogen gas were fixed at 20 sccm, and the pressure in the reactor was fixed 300 Pa.

Figure 2 shows a schematic of the experimental setup. After evacuating the plasma reactor using a rotary pump, Ar gas and H_2 gas were fed into the reactor. The flow rates of Ar and H_2 were controlled with a mass flow controller (Model 3660, KOFLOC). The pressure in the reactor was measured at the upstream and downstream points of the reactor by pressure gauges, and the average value was defined as the system pressure. In those experiments, we measured the amount of H_2O produced by the plasma reduction and the formation rate of H_2O. H_2O that was produced by the reduction reaction of TiO_2 in H_2 plasma was trapped by the liquid-nitrogen cold trap set downstream of the reactor. The accumulated H_2O was measured every 40 min, and the average formation rate of H_2O in a 40-min period was calculated. Also, anatase, rutile and other types of Titanium oxide, such as Ti_2O_3, were detected by means of XRD (X-ray diffraction), and their intensity was used to estimate their quantity.

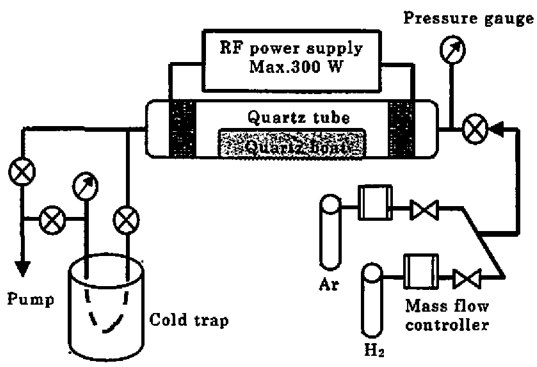

Fig 2. Experimental setup for the partial reduction of TiO_2

3. Results and Discussion

3.1. Small reactor (Reactor S) with continuous-mode RF plasma

The reduction rate of TiO_2 was calculated by measuring the formation rate of H_2O trapped by the liquid nitrogen from the anatase TiO_2 which came into contact with the plasma. The RF discharge power delivered to the plasma in the continuous mode was 90 W.

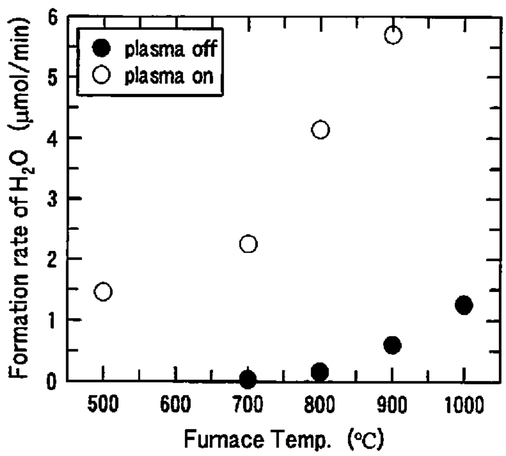

Fig 3. Formation rate of H_2O as a function of the furnace temperature between 500 and 1000℃

Figure 3 shows the formation rate of H_2O as a function of the furnace temperature between 500 and 1000℃. The formation rate of H_2O increased with increasing furnace temperature. Figure 3 implies that the thermal treatment data and plasma treatment data give quite different formation rates of H_2O. The formation rate of H_2O at 500℃ according to the plasma treatment data is almost equal to that at 1000℃ according to the thermal treatment data, which implies that plasma treatment has a strong reduction ability even at lower temperatures. This effect may be the non-equilibrium effect and be caused by the higher density of hydrogen atoms than in the equilibrium state.

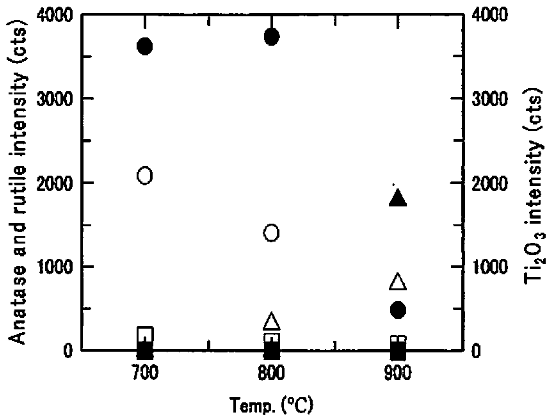

Fig 4. XRD intensity of the reduced TiO_2 as a function of the furnace temperature between 700 and 900℃(The open symbols indicate plasma treatment and The closed symbols indicate thermal treatment. ○anatase, △rutile, □Ti_2O_3)

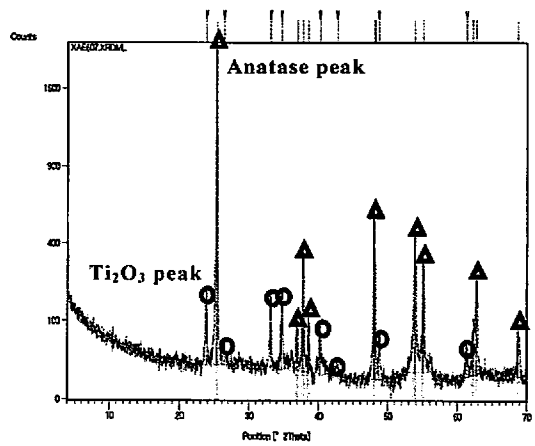

Fig 5. X-ray diffraction patterns of TiO_2 at 700℃ with plasma treatment. A fixed grazing angle of 2° was used. The Circle symbol indicates the Ti_2O_3 peak. The triangle symbol indicates the anatase peak.

Figure 4 shows the XRD analysis of the reduced TiO_2 as a function of the furnace temperature between 700 and 900℃. As shown in Figure 4, at the thermal treatment temperature of 900℃, the anatase peak decreased and the rutile peak emerged. No Ti_2O_3 peak was observed at 700~900℃. In the plasma treatment, however, the anatase peak decreased at temperatures lower than 900℃, and the rutile and Ti_2O_3 peaks were observed simultaneously; the rutile peak was observed at over 800℃, and the Ti_2O_3 peak was observed at 700~900℃. The Ti_2O_3 peak can be seen in Figure 5. This is presumed to be due to the local heating of the sample surface by the high density plasma and discharge power.

3.2. Large reactor (Reactor L) with pulsed-mode RF plasma

The above results indicate that no rutile peak was observed in plasma treatment at 700℃, but that the Ti_2O_3 peak is observed with the anatase peak. This problem is presumed to be due to the local heating of the sample surface by the high density plasma and discharge power. So, we improved the experimental equipment to solve this problem.

Table I. Improvement of the reactor size and control mode of the plasma power

	Reactor S (small)	Reactor L (large)
Control mode	continuous mode	pulsed mode
Tube size (mm^3)	400×φ12	450×φ30
Boat size (mm^3)	50×10×5	150×26×5

Table I shows the improvement of the reactor size and control mode of the plasma input power. We provided plasma input power by controlling it in pulsed mode, while adjusting the reactor size to allow the attainment of a lower reaction temperature on the sample and a lower plasma density. The input power delivered to the plasma in pulsed mode was 0.3, 3, 30, 60 and 90 W. The continuous mode cannot sustain a discharge with small input powers such as 0.3 or 3 W.

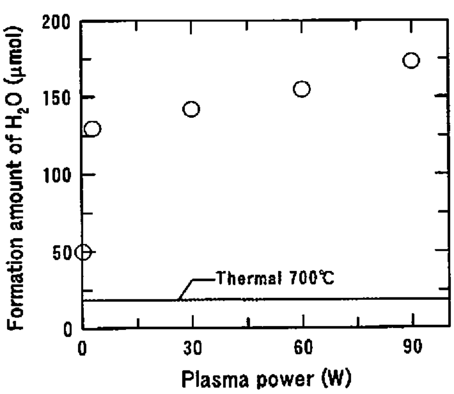

Fig 6. The formation amount of H_2O as a function of the plasma power in pulsed mode at 700℃
(The formation amount of H_2O with thermal treatment at 700℃ was about 20 μmol)

Figure 6 shows the formation amount of H_2O as a function of the plasma power in the pulsed mode at 700℃. As shown in Figure 6, the formation amount of H_2O increased drastically with increasing plasma power. The formation amount of H_2O by plasma treatment in pulsed mode was about 2~8.7 times higher than that by thermal treatment.

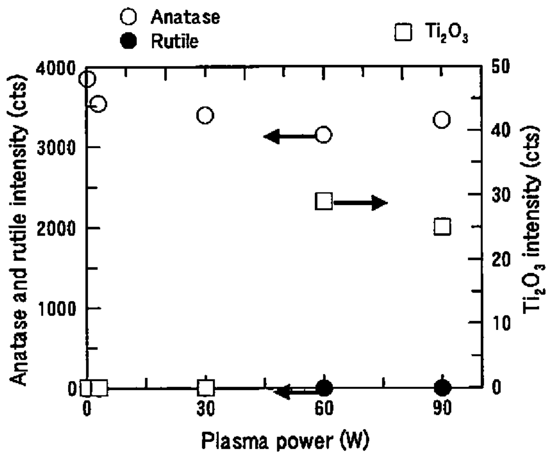

Fig 7. XRD intensity of the reduced TiO_2 as a function of the plasma power in pulsed mode at 700℃ (The anatase and rutile intensities are on the left axis and the Ti_2O_3 intensity is on the right axis)

Figure 7 shows an XRD analysis of the reduced TiO_2 as a function of the plasma power in the pulsed mode at 700℃. As shown in Figure 7, the anatase peak tended to decrease with increasing plasma power. Despite the increasing plasma power, no rutile peak was observed in range of 0.3~90 W. No Ti_2O_3 peak was observed in range of 0.3~30 W, but a small Ti_2O_3 peak was observed at 60 and 90 W. This means that we can obtain a high reduction rate both without form transformation to rutile and without transformation to Ti_2O_3 in the range of 0.3~30 W by controlling the pulsed mode. After the improvement of the experimental equipment, we could successfully achieve the partial reduction of TiO_2, with a higher reduction rate in plasma treatment than in thermal treatment.

4. Conclusion

From the work described in this paper, we can conclude the following:

(1) The formation rate of H_2O increases with increasing furnace temperature and plasma power.

(2) With plasma treatment in continuous mode, no rutile peak is observed at temperatures lower than 800℃, but a Ti_2O_3 peak is observed at 700~900℃.

(3) With plasma treatment in pulsed mode, neither a rutile nor a Ti_2O_3 peak is observed at temperatures lower than 800℃.

(4) Under the proper experimental conditions, we could successfully achieve the partial reduction of TiO_2, and plasma treatment yielded a higher reduction rate, without form transformation to rutile and without transformation to Ti_2O_3.

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