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Studies of the Surface of Titanium Dioxide

II. The Effect of Reduction by Hydrogen on the Weight and the Magnetic Susceptibility

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Simultaneous measurements of weight and magnetic susceptibility of several kinds of titanium dioxide have been carried out after an introduction of hydrogen at temperatures between 400 and 550°C and at pressures between 0.01 and 0.5 atm. The weight of titanium dioxide decreased gradually, while the magnetic susceptibility increased, when hydrogen was introduced above 400°C. It was found that the rate of reduction obeys partly the Elovich equation and that the weight decrease per unit weight of the sample tends to increase with an increase in the specific surface area. It could not be revealed definitely whether the crystal structure of titanium dioxide, rutile or anatase, affects the behavior of the reduction. The activation energy increased gradually with the reduced amount. The magnetic susceptibility increased linearly with a decrease in the weight. These results support the previous findings of the hydrogen reduction of titanium dioxide in connection with the anatase–rutile transformation performed by Shannon. On the basis of these results, the reduction mechanism was discussed and the rate-determining step in the initial stage was presumed to be formation of the surface hydroxyl groups followed by rapid removal of water molecules from the surface.

INTRODUCTION

It is well known that titanium dioxide becomes oxygen deficient by evacuation or contact with such a reducing gas as hydrogen at elevated temperature. It was shown in a previous paper (*1*) that the removal of oxygen atoms from titanium dioxide by hydrogen reduction causes a marked change in the surface properties of tianium dioxide, such as the heat of immersion in water. Though a number of studies on the physical and chemical properties of the reduced state of titanium dioxide have been made (*2–4*), quantitative details of the kinetics of the hydrogen reduction have not been reported.

The hydrogen reduction of titanium dioxide causes a removal of part of the oxygen atoms as water molecules, producing a defect structure such as oxygen vacancies rather than interstitial titanium ions (*5*). The selective production of oxygen vacancies in titanium dioxide during hydrogen reduction has been inferred by Shannon in connection with an acceleration effect of hydrogen atmosphere on the anatase–rutile transformation (*5,6*). The electrons which are produced by the removal of oxygen atoms can reside in the vacancies in conjunction with titanium ions in the lattice or move around the crystal as free electrons. These electrons may influence significantly the magnetic properties of the reduced titanium dioxide (*4,7,8*). Therefore, it is of interest to compare the weight change and the magnetic susceptibility during the hydrogen reduction and, further, to compare the results with those on the anatase–rutile transformation kinetics reported (*5,6*).

In this study changes in the weight and the magnetic susceptibility were measured simultaneously after hydrogen was introduced at several temperatures and pressures. The effects of the surface area and crystal modification on the behavior of the reduction were examined for several kinds of samples and, in addition, the mechanism of hydrogen reduction was interpreted, based on the results of the activation energy and the relation between changes in the magnetic susceptibility and the weight.

EXPERIMENTAL METHODS

Materials

Several kinds of titanium dioxide samples were used. The preparation, crystal structure, and surface area of the samples are listed in Table 1. The methods of purification of the samples were described in previous papers (*1,9,10*). Samples R-II and A-I were mainly examined in this study.

Procedure

Both weight and magnetic susceptibility were measured by the use of a Cahn RG electrobalance. The apparatus is shown schematically in Fig. 1. About 155 mg of titanium dioxide was charged in a quartz bucket and a similar amount of fused quartz was placed in the other bucket as a counterweight. In order to minimize the thermomolecular effect, two similar furnaces of no induction were used.

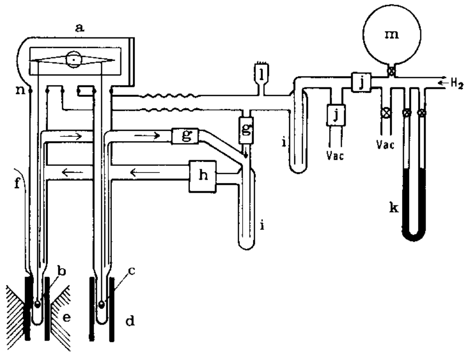


FIG. 1. Experimental apparatus for studying the hydrogen reduction. (a) Cahn RG electrobalance, (b) sample, (c) fused quartz, (d) electric furnace, (e) magnetic pole, (f) thermocouple, (g) platinum asbestos, (h) glass fan, (i) liquid nitrogen trap, (j) high vacuum metal cock, (k) Hg manometer, (l) ionization gauge, (m) hydrogen reservoir, and (n) O-ring

The sample was evacuated at 500°C and 10^{-5} Torr for 2 hr, exposed to oxygen of 0.2 atm at 500°C, and then evacuated for 2 hr more at the same temperature. Then, hydrogen at pressures between 0.01 and 0.5 atm was introduced at temperatures between 400 and 550°C; the hydrogen had been purified by passing it through plat-

TABLE 1

PREPARATION, CRYSTAL STRUCTURE, AND SURFACE AREA

Sample	Preparation method	Crystal structure	Surface area (m^2/g)
R-I	Hydrolyzed titanium tetrachloride in aqueous media and calcined at 600°C for 6 hr in a stream of oxygen	Rutile	18.5
R-II	Prepared in the same manner as R-I	Rutile	11.7
R-III	The same as R-I but calcined at 800°C for 4 hr in a stream of oxygen	Rutile	4.6
A-I	Hydrolyzed titanium sulfate in aqueous media	Anatase	144
A-II	Calcined A-I at 750°C for 20 hr in air	Anatase[a]	6.5
A-III	Hydrolyzed titanium isopropoxide and calcined at 550°C for 10 hr in a stream of oxygen	Anatase	56
S	Single crystal grown by the Verneuil method	Rutile	

[a] This sample contains less than 1% rutile phase, though transformed to rutile about 50% when calcined at 900°C for 20 hr in air.

inum asbestos and a liquid nitrogen trap. The blank test was carried out by employing fused quartz instead of titanium dioxide sample or by introducing helium in place of hydrogen at various temperatures and pressures.

The hydrogen introduced in the system was circulated with the aid of a glass fan through both platinum asbestos and a liquid nitrogen trap as shown in Fig. 1. No grease was used in the system in order to avoid organic contaminants (*1*). A change in the pressure was negligible throughout the run, since the volume of the system was larger than 3 liters. The magnetic susceptibility was determined by the Faraday method; the magnetic field ranged from 3600 to 5000 G. As a calibration agent, sucrose was employed (*11*). The magnetization of the sample was found to be proportional to the magnetic field. The simultaneous determinations of the weight and the magnetic susceptibility were carried out by repeating application and removal of the magnetic field alternately.

RESULTS AND DISCUSSION

Defect Structure of Hydrogen-Reduced Titanium Dioxide

When titanium dioxide is evacuated at around 500°C, most of the hydroxyl groups on the surface are removed as water molecules, resulting in the formation of the oxide structure on the surface (*9*). Moreover, the presence of Ti^{3+} ions on the surface of titanium dioxide is indicated by ESR measurements confirms the reduction even by evacuation at 500°C (*12*). By the introduction of hydrogen at a high temperature, some oxygen atoms on the surface are first removed, producing oxygen vacancies and Ti^{3+} ions on the surface, while the formation of the hydroxyl ions at the lattice oxygen ion sites in the bulk results from the interaction of the oxygen ions with protons which penetrate into the interior during hydrogen reduction (*5*). Then, these oxygen vacancies on the surface spread into the bulk through easy exchange with the hydroxyl ions because they encounter less of an energy barrier than oxygen ions when jumping from an occupied site to a vacancy owing to their lower ionic charge and almost identical ionic radius (*5*). This hypothesis of Shannon (*5*) that the oxygen vacancies migrate from the surface into the bulk has recently been supported by Iyengar *et al.* (*13*) by examining the O_2^- radicals on reduced rutile by ESR measurements. Further, it was found that the transition of anatase to rutile is enhanced when anatase is heated in an atmosphere of hydrogen but retarded when heated *in vacuo* (*5,6*). The oxygen vacancies present in titanium dioxide have been considered also by Shannon (*5*) to be responsible for acceleration of the transformation because of the low energy to form the new structure by collapsing the anatase open structure: reduction of the number of Ti–O bonds and the strain energy which must be overcome to deform the structure. On the other hand, interstitial Ti^{3+} ions which are produced by the heating *in vacuo* inhibit the transformation because they increase the strain energy.

Variations of Weight and Magnetic Susceptibility with Kinds of Samples

The decrements in weight of the various kinds of titanium dioxide by the introduction of hydrogen at 0.5 atm and 500°C are shown in Fig. 2 as a function of time. It took more than 500 min to reach the reduction equilibrium. It is obvious from Fig. 2 that the weight decrease is inclined to increase with an increase in the specific surface area. In the case of single crystal, however, there was no appreciable change in the weight even after 600 min. These results indicate that the surface of the titanium dioxide plays an important role in the reduction process. The role of the surface may be clarified by evaluating the

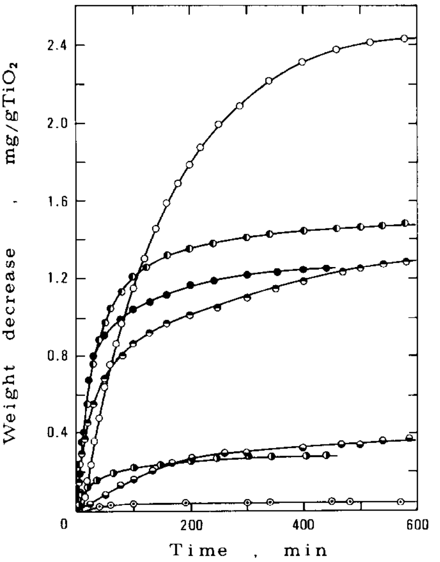


FIG. 2. Decrease in weight of titanium dioxide as a function of time after the introduction of hydrogen at 0.5 atm and 500°C: (◐) R-I, (●) R-II, (◑) R-III, (○) A-I, (◒) A-II, (◓) A-III, (○) S.

reduced amounts on the basis of the surface area. The concentration of oxygen atoms on the surface, calculated on the assumption of the stoichiometric composition for the surface layer, is 20.8/100 Å^2 for rutile (*14*) and 11.3/100 Å^2 for anatase (*1*); the former surface is composed of (110), (101), and (100) planes and the latter (101), (001), and (100) planes. In Table 2 are given the weight decrease near the equilibrium, the number of oxygen atoms removed per unit surface area, and the percentage of oxygen atoms removed from the surface. From the third column it seems, in appearance, that the rutile form is more easily reduced than anatase because of the larger density of oxygen atoms on the surface of the former. The larger reduced amount of A-II than other anatase samples might be responsible for the presence of rutile phase to some extent on the surface. However, the reduced amount per unit surface area tends to decrease with an increase in the specific surface area except for the samples A-II, R-III, and single crystal. The surface areas of A-I and A-III are markedly larger than others, indicating the lower crystallinity. The retardation of the anatase–rutile transformation has been found for the samples containing sulfate or phosphate ion as an impurity which is considered to lower the crystallinity (*6*) and also to reduce the concentration of the vacancies (*6*). The lower reduced amounts of A-I and A-III may be responsible for the lower crystallinity of the surface. In these samples as well as A-II after the hydrogen reduction, however, no trace of rutile phase could be ascertained by X-ray analysis. Nevertheless, the transformation would have occurred which could not be detected owing to the low amount of rutile phase or to its presence near the surface region since the rutile phase is nucleated on the surface and then spreads into anatase (*15*). It can not be learned from Table 2 whether the reduced amount depends on the crystal structure or the surface area. It appears in Fig. 2 that rutile comes to equilibrium faster than anatase, irrespective of the surface area.

TABLE 2
REDUCED AMOUNT OF TITANIUM DIOXIDE AT 500°C

	Reduced amount			Magnetic susceptibility before reduction
Sample	mg/g TiO$_2$	oxygen atoms/ 100 Å^2	%	($\times 10^{-8}$ unit)
R-I	1.49	3.0	14.6	7.6
R-II	1.26	4.0	19.5	7.5
R-III	0.28	2.3	11.1	7.4
A-I	2.45	0.6	5.3	5.9
A-II	0.38	2.2	18.3	23.3
A-III	1.30	0.9	7.28	13.1
S	0.048	—	—	1.1

The fourth column in Table 2 shows that removed oxygen atoms range from 5 to 20% of the total, if the elimination of oxygen atoms is limited to the surface. Then, the composition from $TiO_{1.89}$ to $TiO_{1.62}$ can be obtained for the surface layer. The real surface of reduced titanium dioxide, however, may have fewer oxygen vacancies than those calculated above since the reduction region may not be restricted to the top layer of the surface, as has been reported by Richardson *et al.* (*16*) and Iyengar *et al.* (*13*). The rate of decrease in the weight of titanium dioxide was found to obey the Elovich equation which has been widely applied to surface phenomena.

The increments of the magnetic susceptibilities of various kinds of titanium dioxide after the introduction of hydrogen at 500°C and 0.5 atm are shown in Fig. 3 as a function of time. The magnetic susceptibility of the sample A-II showed a remarkably high value, 4.2×10^{-7} unit, immediately after hydrogen was introduced and then decreased gradually with time; this is not shown in Fig. 3. The degree of increase in the magnetic susceptibility of each sample did not coincide with the corresponding weight decrease which has been shown in Fig. 2. However, the rate of increase in the magnetic susceptibility was found to obey also the Elovich equation. The values of the magnetic susceptibility of the samples evacuated at 500°C before the introduction of hydrogen are indicated in the last column in Table 2. The differences in these values may be attributed to a minute amount of impurity present in the solid and/or to the reduced state of the surface. The magnetic susceptibility of rutile indicated in Table 2 was little affected by temperature between −196 and 25°C and showed the value analogous to those reported by Gray *et al.* (*4*) and Senftle and Pankey (*17*).

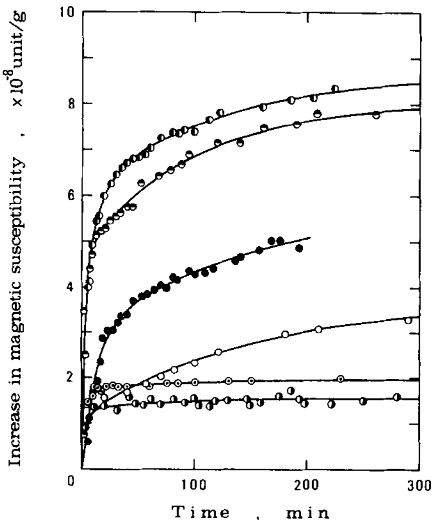


FIG. 3. Increase in magnetic susceptibility of titanium dioxide as a function of time after the introduction of hydrogen at 0.5 atm and 500°C: (◐) R-I, (●) R-II, (◑) R-III, (○) A-I, (◓) A-III, (○) S.

Dependences of the Reduction on Temperature and Pressure

In order to examine the reduction process in further detail, the dependence of the weight decrease on temperature and pressure was measured for the samples R-II and A-I. The results of the temperature dependency at 0.5 atm are shown in Fig 4a and b, respectively. As shown in the figure, the rate of reduction at initial stage and the weight decrease increased with an increase in temperature. No weight decrease appeared at temperature lower than 350°C for R-II and 400°C for A-I. The induction period occurred at low temperature and decreased with a rise in temperature. The decrements of weights of both samples at reduction equilibrium seems to be dependent on temperature.

The dependence of the reduction of R-II and A-I on the pressure of hydrogen at 500°C is shown in Fig. 5 as a function of time. The rate of decrease in weight increased with an increase in pressure. Further, the pressure dependence of rutile is larger than that of anatase.

The rates of decrease in weights of R-II and A-I at several temperatures were obtained by differentiating the curves in Fig. 4a and b, respectively. The results are given, respectively, in Fig. 6a and b as a function of the weight decrease. The rate of reduction obeys the following Elovich equation though distinct breaks occur in the plots:

$$dq/dt = a \exp(-bq), \qquad (1)$$

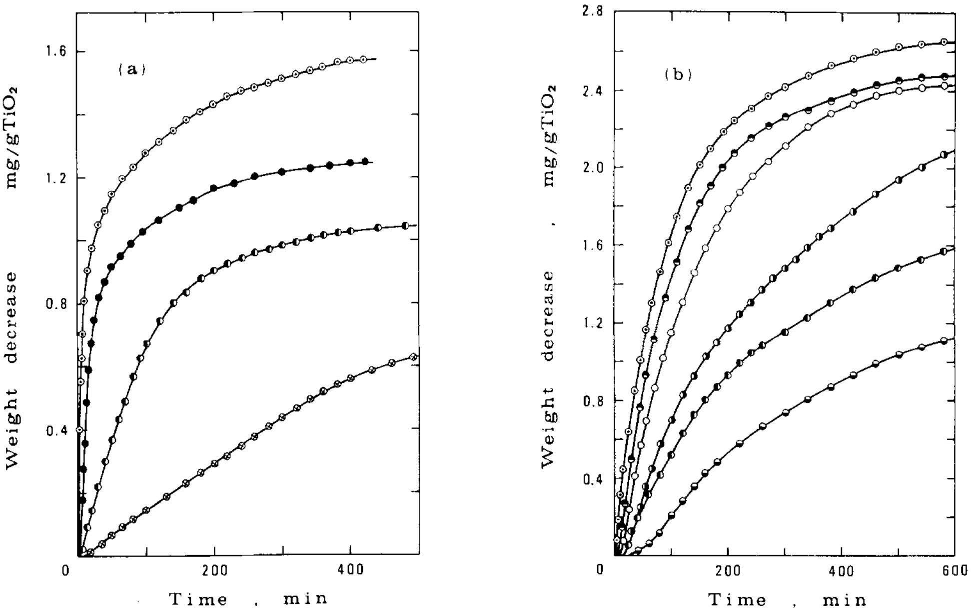


FIG. 4. Temperature dependence of weight decrease after the introduction of hydrogen at 0.5 atm; (a) rutile (R-II) (°C): (⊗) 400, (◐) 450, (●) 500, (⊙) 550; (b) anatase (A-I) (°C): (⊖) 425, (◐) 450, (◑) 475, (○) 500, (◓) 525, (⊙) 550.

where q is the weight decrease at time t. The constants, a and b, are given, respectively by

$$a = (KRT/\alpha)\exp(-E_0/RT), \qquad (2)$$

$$b = \alpha/RT, \qquad (3)$$

where K is a pressure-dependent constant, R the gas constant, T the absolute temperature, α a constant, and E_0 the activation energy at the start of reduction. The slope of these plots, b, changed at particular weight decrease, that is, at 0.45 and 0.8 mg/g for rutile and at 0.2 and 1.9 mg/g for anatase. This suggests that the hydrogen reduction of titanium dioxide has different stages depending on the degree of reduction; this stage might be responsible for the diffusion of the oxygen vacancies into the interior near the surface probably associated with the anatase–rutile transformation.

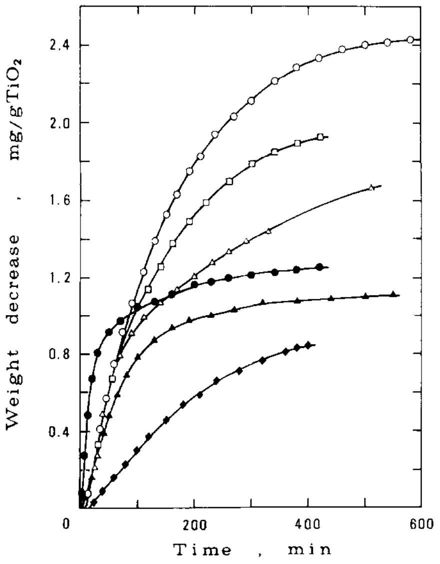


FIG. 5. Pressure dependence of weight decrease after the introduction of hydrogen at 500°C; rutile (R-II) (atm): (●) 0.5, (▲) 0.05, (◆) 0.01; anatase (A-I) (atm): (○) 0.5, (□) 0.25, (△) 0.05.

The rate of reduction increased in proportion to $P^{0.6-0.7}$ in the range of weight decrease from 0 to 0.9 mg/g for rutile and $P^{0.15-0.19}$ from 0.6 to 1.0 mg/g for anatase. Since the adsorption of hydrogen on the surface depends on the pressure, it is suggested that the reduction process may be correlated with the amounts of hydrogen adsorbed on the surface of titanium dioxide.

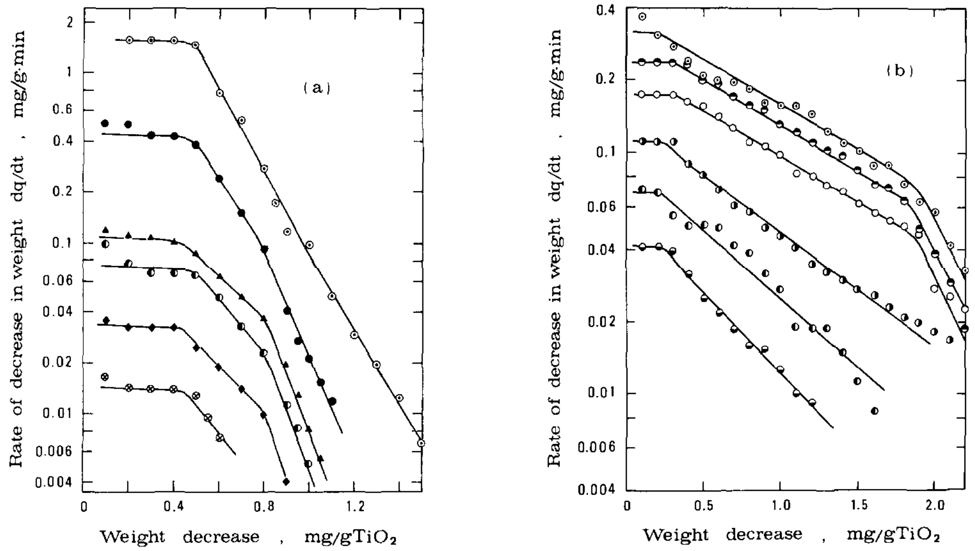


FIG. 6. Rate of decrease in weight as a function of the weight decrease: (a) rutile (R-II) (°C): (⊗) 400, (◐) 450, (●) 500, (⊙) 550, (▲) 500 (0.05 atm), (◆) 500 (0.01 atm); (b) anatase (A-I) (°C): (◒) 425, (◐) 450, (◑) 475, (○) 500, (◓) 525, (⊙) 550.

The magnetic susceptibility of both samples changed also with temperature and pressure according to the degree of weight decrease in a similar way as has been shown in Fig. 3.

Activation Energy

The activation energies of the hydrogen reduction for R-II and A-I were obtained, respectively, from Fig. 6a and b by using Eqs. (1) and (2) and the following relation:

$$dq\,/\,dt = A\exp(-E_a/RT), \qquad (4)$$

where E_a is the activation energy at any degree of reduction and A is a constant. The results are given in Fig. 7 as a function of the weight decrease. As for the sample A-I, E_a takes two different values according to the temperature region: it is lower above 500°C than below that. At high temperatures above 500°C, a spontaneous removal of oxygen from A-I may also take place, resulting in a extra decrease in weight. The activation energy depends on the weight decrease, since

$$E_a = E_0 + \alpha q. \qquad (5)$$

The slope of these plots, α, changes abruptly in analogy with the case of the rate of reduction which has been shown in Fig. 6. According to the theoretical interpretations of the Elovich equation (*18*), these results imply a heterogeneous distribution of oxygen atoms which are to be removed from the surface for anatase and

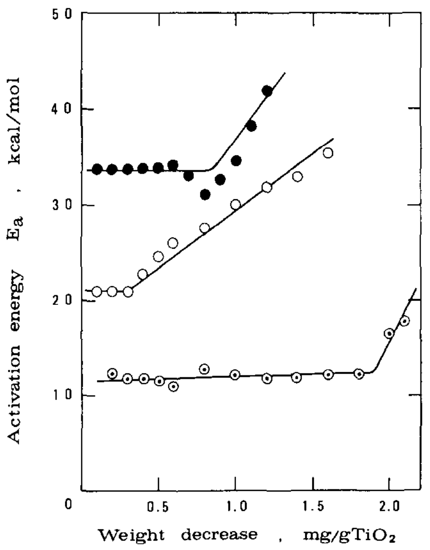


FIG. 7. Activation energy of the reduction of titanium dioxide by hydrogen: (●) rutile (R-II), (⊙) anatase (A-I) above 500°C; (○) anatase (A-I) below 500°C.

a homogeneous region in part for rutile. A rapid decrease in the rate of reduction of anatase when the reduction proceeds to considerable degree above 500°C, as shown in Fig. 6, suggests deformation of the surface structure because of a slight decrease in surface area above 525°C, though rutile showed no change in surface area even after reduced at 550°C.

The activation energies obtained for both samples in the initial stage are too low to explain the removal of oxygen by the diffusion of oxygen in the bulk, the activation energy of which has been reported to be 60 kcal/mol (*19*). The diffusion-controlled reaction is expressed by the parabolic rate law which cannot be applicable for this reaction. The activation energy of the anatase–rutile transformation in air was obtained to be above 100 kcal/mol (*6*) and would be lowered markedly in the atmosphere of hydrogen.

Relation between Magnetic Susceptibility and Reduced Weight

The magnetic susceptibility of titanium dioxide increased progressively as reduction proceeds, as shown in Figs. 2 and 3. The relation between an increase in the magnetic susceptibility and the weight decrease is shown in Fig. 8 for various kinds of titanium dioxide. The broken line in Fig. 8 represents a calculated relation between the magnetic susceptibility at 500°C and the weight decrease, based on the assumptions that all electrons produced by the removal of oxygen atoms reside on titanium ions, resulting in the formation of Ti^{3+} even at high temperatures and that these electrons exhibit Langevin paramagnetism with an effective magnetic moment of 1.73 μ_B (*20*). In practice, however, most of the electrons produced behave as free electrons at a high temperature. In general, the contribution of conduction electrons in metals to paramagnetic susceptibility is remarkably small, which is known as the Pauli spin susceptibility (*21*), and so an increase in the magnetic susceptibility caused by hydrogen reduction can not be interpreted by this mechanism. It may be considered, therefore, that the conduction electrons in titanium dioxide contribute to the magnetic susceptibility in the same manner as the unpaired electrons in nonin-

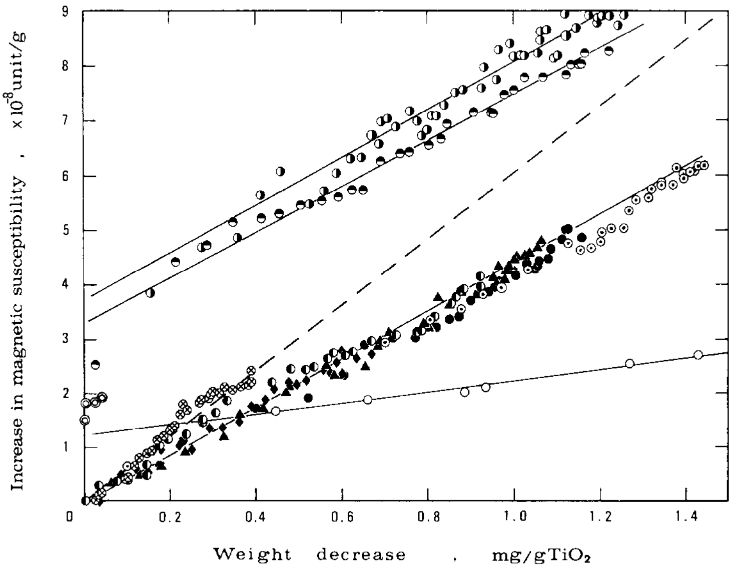


FIG. 8. Relation between the magnetic susceptibility and the weight decrease: (◑) R-I, (⊙) R-II (550°C), (●) R-II, (◐) R-II (450°C), (⊗) R-II (400°C), (▲) R-II (0.05 atm), (◆) R-II (0.01 atm), (○) A-I, (◒) A-III, (◎) S.

teracting hydrogen-like donors, since their effective mass is considerable (*2*).

It is to be noted that the increment of the magnetic susceptibility obtained experimentally is a linear function of the decrement of the weight, though the slope is different from sample to sample. The increment of the magnetic susceptibility is responsible not only for the temperature-dependent paramagnetism, but also for the temperature-independent one. From the measurements of the temperature dependence of the magnetic susceptibility between −196 and 25°C (*22*), it was found that the contribution of the latter is about 40% at 25°C and exceeds 60% at 500°C. The temperature-independent paramagnetism of the Magnéli phases of Ti–O system has been found to increase with a departure from the stoichiometric composition (*23*). As shown in Fig. 8, an initial increase in magnetic susceptibility appears in most of the samples; this result indicates the presence of hydrogen which is adsorbed on the surface and penetrates in the bulk, supporting the previous finding that the hydroxyl groups are formed when hydrogen is introduced (*5*). It is interesting that the rutile single crystal has a large magnetic susceptibility though the weight decrease is negligibly small.

Mechanism of Reduction by Hydrogen

The process of the hydrogen reduction of titanium dioxide can be summarized as follows:

a. Adsorption of hydrogen molecules on the surface;

b. Dissociation of the adsorbed hydrogen molecules into atoms, and

b′. Penetration of some hydrogen atoms or ions in the interior;

c. Formation of hydroxyl groups on the surface, followed by the production of oxygen vacancies, and

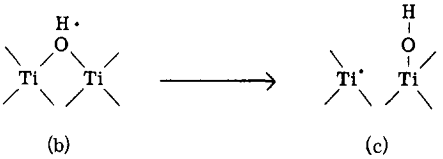
c′. Formation of hydroxyl ions in the interior;

d. Condensation of the surface hydroxyl groups, resulting in the production of water molecules, and

d′. Diffusion of the oxygen vacancies on the surface inward by the exchange with hydroxyl ions in the bulk and then production of water molecules on the surface;

e. Desorption of the water molecules from the surface.

The observed stage of the actual decrease in weight of titanium dioxide is represented by the step (e). The steps (b), (b′), (c) and (c′) may contribute to an increase in the magnetic susceptibility. In the step (c), the unpaired electron on titanium atom is produced by Ti–O bond cleavage as may be represented in the following scheme:



From the experiment of hydrogen–deuterium equilibration reaction on the surface of rutile, the activation energy for the reaction was obtained to be about 10 kcal/mol (*24*). On the other hand, the activation energy for the desorption of the chemisorbed water on the surface of rutile was given to be 25.6 kcal/mol from the measurement of temperature-programmed desorption (*25*). Further, a linear relationship was found to hold between the magnetic susceptibility and the weight decrease, as shown in Fig. 8. From these results, it can be proposed that the rate-determining step of the initial stage of the reduction reaction by hydrogen is step (c). Therefore, after the reduction proceeds to a considerable extent on the surface, the diffusion of oxygen vacancies into the interior and probably the anatase–rutile transition in the case of anatase may affect the rate of reduction of the titanium dioxide. The difference in the reduction behaviors of various kinds of samples may be due to that in the structure and character of Ti–O bond on the surface and in the bulk, which may also depend on the preparation and the sintering of the samples.

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