Reduction of titanium oxide in the presence of nickel by nonequilibrium hydrogen gas

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We investigated the reduction of TiO₂ in the presence of Ni by nonequilibrium hydrogen gas, including low-temperature hydrogen plasma at 800 °C and supercooled monatomic hydrogen at 1000 °C. TiO₂ was reduced to Ti₂O₃, which is not in equilibrium phase, by low-temperature hydrogen plasma. The results of x-ray diffraction and energy dispersive x-ray analysis in experiments at 1000 °C indicate that the thermodynamical reduction potential of supercooled monatomic hydrogen is almost the same as atmospheric hydrogen gas. However, the wide Ti₃O₅ layer formed only in the case of the reduction at 1000 °C by supercooled monatomic hydrogen. With these experimental facts, we speculate that the reduction mechanism by nonequilibrium hydrogen consists of two steps; the releasing energy process and the relaxation process. We can explain the difference of reduction products by nonequilibrium hydrogen gas on the assumption of the rate of the relaxation process between 800 and 1000 °C.

I. INTRODUCTION

Titanium alloys are attractive materials because they have various unique properties. Ni–Ti alloy shows shape memory and a superelasticity effect. The Nb–Ti alloy is a superconducting material. Some titanium alloys show excellent corrosion resistance and heat resistance. However, such materials are expensive. One of the reasons is that they are made from an alloy metal and pure titanium, which is an expensive material because of its high production cost. The major production process of titanium is the Kroll process, which consists of carbochlorination of TiO₂, purification of TiCl₄, magnetothermic reduction of TiCl₄ to metallic titanium, and vacuum distillation of MgCl₂ and excess Mg from metallic titanium. This process has problems of process complication, low productivity of titanium, and high energy consumption. Therefore, direct reduction of titanium oxide to titanium alloy has an advantage of simplicity. Reduction by hydrogen gas may be the simplest process because the only by-product is water vapor. In this study, the reduction of titanium oxide in the presence of nickel as the alloying element to titanium alloy by hydrogen gas was investigated.

II. THERMODYNAMICS OF Ti–Ni–O TERNARY SYSTEM

Figure 1(a) shows the equilibrium chemical potential of oxygen, RT ln pO₂, in equilibrium with some titanium oxides as a function of temperature, T, under the conditions that activities of substances in condensed phases are unity. Here, R is the gas constant, and p_i is the partial pressure of chemical species, i. RT ln pO₂ in equilibrium with H₂ of 1 atm and H₂O of 1 atm or 10⁻⁴ atm are also shown in Fig. 1. Figure 1(b) shows RT ln pO₂ in equilibrium with titanium oxides and Ti–Ni alloys and RT ln pO₂ in equilibrium with H (monatomic hydrogen) of 1 atm and H₂O of 1 atm. The lines in Fig. 1(b) will be discussed later. From the figure, when RT ln pO₂ in equilibrium with H₂ and H₂O is lower than that with Ti and TiO₂, TiO₂ can be reduced to Ti by hydrogen. But the...
figure indicates that it is very difficult to obtain Ti by hydrogen reduction. We empirically know that it is not easy to decrease the partial pressure of H$_2$O, $P_{H_2O}$; in the gas boundary layer near titanium oxides below $10^{-4}$ atm during hydrogen reduction. Consequently, we have to give up on reducing titanium oxide to pure metallic titanium. Instead of obtaining pure titanium, we tried to reduce titanium oxide to an alloy.

The reduction of TiO$_2$ to Ti by hydrogen is expressed by Eq. (1), and its Gibbs energy change, $\Delta G$, is represented by Eq. (2).

$$\text{TiO}_2 + 2H_2 \rightarrow \text{Ti} + 2H_2O, \quad (1)$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{Ti}}^2p_{H_2O}^2}{a_{\text{TiO}_2}p_{H_2}^2} = \Delta G^\circ + 2.303 RT \times (\log a_{\text{Ti}} + 2\log p_{H_2O} - \log a_{\text{TiO}_2} - 2\log p_{H_2}) \quad , \quad (2)$$

where $\Delta G^\circ$ is the standard Gibbs energy change. The value of $\Delta G$ is positive under normal conditions, but might become negative by decreasing $a_{\text{Ti}}$ and $p_{H_2O}$, or increasing $a_{\text{TiO}_2}$ and $p_{H_2}$. It is difficult to decrease $p_{H_2O}$ to below $10^{-4}$ atm, and to increase $a_{\text{TiO}_2}$ to above unity. Thus, to make the value of $\Delta G$ negative, it is necessary to decrease $a_{\text{Ti}}$ and/or increase $p_{H_2}$.

The activity of titanium in alloy is lower than that of pure titanium, which means that alloying with other metal leads to a decrease in $a_{\text{Ti}}$. In the presence of an alloy element, which has a strong affinity with titanium, titanium oxide might be reduced to titanium alloy in reduction by hydrogen gas. In fact, the reduction of TiO$_2$ in the presence of platinum by hydrogen gas has been confirmed by Meschter and Worrel, and Shioi et al. Whether or not the reaction proceeds depends on the affinity between titanium and the alloy element. We estimate the affinity from the formation enthalpy of the titanium alloy. Nickel is selected as an appropriate element for this study because the affinity between titanium and nickel is relatively strong; the formation enthalpy of Ni$_3$Ti is $-152.2 \text{ kJ mol}^{-1}$.

As a way of increasing $p_{H_2}$, the use of nonequilibrium hydrogen gas, including hydrogen plasma or supercooled monatomic hydrogen, is considered. Some researchers attempted reduction of titanium oxide by hydrogen plasma. Although they have not obtained metallic titanium with hydrogen plasma reduction, Huet et al. reported that TiO$_2$ could be reduced to TiO at about 800 °C by low-temperature hydrogen plasma. TiO cannot be obtained through reduction of TiO$_2$ by atmospheric hydrogen gas under normal conditions. Therefore, these results clearly indicate that low-temperature hydrogen plasma is a stronger reductant than atmospheric hydrogen gas.

From the background described previously, we were motivated to examine the combination of these ways to obtain titanium alloy from a mixture of titanium oxide and nickel. In this study, we thus investigate the reduction of titanium oxide by low-temperature hydrogen
plasma or by supercooled monatomic hydrogen in the presence of nickel.

The phase diagram of the Ti–Ni–O ternary system at 927 °C is shown in Fig. 2(a). Figure 2(b) is a schematic illustration showing the equilibrium phase relationship between titanium oxides and nickel in detail. Ni(ss) means solid solution of nickel phase. It does not have solubility of titanium when Ni(ss) and Ti4O7 are in equilibrium, whereas Ni(ss) has solubility of 3 at.% titanium when Ni(ss) and Ti3O5 are in equilibrium. The upper limit of the solubility of titanium in Ni(ss) is 11 at.%, when Ni(ss), Ti2O3, and Ni3Ti are in equilibrium. On the other hand, we can know the extent of activity of titanium in a system from the concentration of Ti in Ni(ss). This information will be a key for analyzing the reduction potential of supercooled monatomic hydrogen in Sec. V. A.

The chemical potential diagram of the Ti–Ni–O ternary system is shown in Fig. 3. This diagram was made using the standard Gibbs energy of formation at 1000 °C. Three axes show the chemical potentials of titanium, nickel, and oxygen. Here, each chemical potential can be represented by log $a_{Ti}$, log $a_{Ni}$, and log $p_{O2}$ in Fig. 3. It is assumed that each solid phase has no solubility of other elements except for $\alpha$-Ti, $\beta$-Ti, and Ni(ss). The $\alpha$-Ti

![Diagram](image-url)

FIG. 2. (a) Isothermal cross section of phase diagram of Ti–Ni–O ternary system at 927 °C.10 (b) Schematic view of phase relation between titanium oxides and Ni(ss), as shown by dashed line in (a).

![Diagram](image-url)

(a) T = 1000 °C

(b) T = 1000 °C

FIG. 3. (a) Chemical potential diagram of Ti–Ni–O system at 1000 °C. (b) Projection view to log $p_{O2}$ – log $a_{Ti}$ plane. [Barin], [Liang], and [Chattopadhyay] correspond to the phase boundary line between Ni(ss) and Ni3Ti calculated with the reported Gibbs energies of formation of Ni3Ti. Dashed line shows the chemical potential of oxygen in equilibrium with hydrogen gas of 1 atm and water of 10 atm.
and β-Ti are considered to be solutions of titanium and oxygen, and Ni(ss) is considered to be a solution of nickel and titanium. The thermodynamic information of such solid solution was taken from the literature. Three different Gibbs energies of formation are reported for Ni$_3$Ti. [Barin], [Liang], and [Chattopadhyay] correspond to the phase boundary line between Ni(ss) and Ni$_3$Ti calculated with the thermodynamic data described by Barin, Liang et al., and Chattopadhyay et al., respectively. From this figure, if we can reduce the partial pressure of oxygen to allow the formation of TiO, Ni$_3$Ti can be obtained in the presence of nickel. The dependency of the chemical potential of oxygen on temperature is shown in Fig. 1(b). There is a possibility that TiO forms at 1000 °C as reported by Huet et al.

III. EXPERIMENTAL

Rutile type TiO$_2$ powder (99.9%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and Ni powder (catalyst grade, Fukuda Metal Foil and Powder Co., Ltd., Kyoto, Japan) were mixed at an atomic ratio of 1 to 3 by ball milling for 8 h. The mixed powder was then pressed at 412 or 103 MPa into the pellet. Reduction experiments were carried out using these sample pellets. The size of the sample pellets and experimental conditions are listed in Table I. P1 was reduced at 800 °C by low-temperature hydrogen plasma generated with radio frequency (rf) plasma equipment under the $p_{H_2}$ of 10$^{-3}$ atm for 6 h. F1 and F2 are the reduction experiments by supercooled monatomic hydrogen. In this study, the hot-wire method was adopted for making supercooled monatomic hydrogen. Figure 4 shows a schematic illustration of the experimental apparatus. Hydrogen gas was generated by electrolysis of deionized water and was purified with a permeating palladium membrane. Purified molecular hydrogen was then introduced from the top of the reactor, which was made from stainless steel, SUS316, and protected from thermal oxidation by argon gas. A part of the molecular hydrogen was dissociated to monatomic hydrogen by a tungsten filament heated at 2000 or 2500 °C by supplying direct current (dc) from the dc source. The filament temperature was maintained at 1000 °C in the stainless steel tube. Reduction experiments by atmospheric hydrogen gas, U1 and U2, were also carried out using the same apparatus. In these cases, the filament was not heated.

The product phase of each sample pellet after reduction was identified by a 20/0 scan of x-ray diffraction (XRD; RINT2200, Cu K$_\alpha$, Rigaku Corporation, Tokyo, Japan). The product phase in the surface layer was identified by grazing incidence XRD (GI-XRD; GI-XRD; Cu K$_\alpha$, X'Pert MRD, PANalytical, Almelo, The Netherlands), where the incident angle of x-ray against the surface of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature, $T^\circ$C</th>
<th>Treatment time, $t$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>800</td>
<td>6</td>
</tr>
<tr>
<td>F1</td>
<td>1000</td>
<td>12</td>
</tr>
<tr>
<td>F2</td>
<td>1000</td>
<td>12</td>
</tr>
<tr>
<td>U1</td>
<td>800</td>
<td>6</td>
</tr>
<tr>
<td>U2</td>
<td>1000</td>
<td>12</td>
</tr>
</tbody>
</table>

### TABLE I. Sample pellet prepared for the experiments and the reduction conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure, $p$/MPa</th>
<th>Diameter, $r$/mm</th>
<th>Thickness, $d$/mm</th>
<th>Weight, $w$/mg</th>
<th>Reductant</th>
<th>Temperature, $T$°C</th>
<th>Treatment time, $t$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>103</td>
<td>11</td>
<td>2.4</td>
<td>$8.4 \times 10^2$</td>
<td>Low temperature hydrogen plasma</td>
<td>800</td>
<td>-</td>
</tr>
<tr>
<td>F1</td>
<td>412</td>
<td>11</td>
<td>0.2</td>
<td>$7.0 \times 10$</td>
<td>Supercooled monatomic hydrogen</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td>F2</td>
<td>412</td>
<td>11</td>
<td>0.4</td>
<td>$2.5 \times 10^2$</td>
<td>Supercooled monatomic hydrogen</td>
<td>1000</td>
<td>2500</td>
</tr>
<tr>
<td>U1</td>
<td>412</td>
<td>11</td>
<td>0.3</td>
<td>$1.2 \times 10^2$</td>
<td>Atmospheric hydrogen gas</td>
<td>800</td>
<td>-</td>
</tr>
<tr>
<td>U2</td>
<td>412</td>
<td>11</td>
<td>0.2</td>
<td>$7.1 \times 10$</td>
<td>Atmospheric hydrogen gas</td>
<td>1000</td>
<td>-</td>
</tr>
</tbody>
</table>
the sample pellet was 1°. The composition in the nickel phase was measured by energy-dispersive x-ray spectrometer (EDX; JED-2300, JEOL, Tokyo, Japan) with field-emission scanning electron microscopy (FE-SEM; JSM-6500F, JEOL).

IV. RESULTS
A. Reduction by low-temperature hydrogen plasma

The photographs and SEM image of the sample pellet before and after the reduction experiment at 800 °C by low-temperature hydrogen plasma (P1) and atmospheric hydrogen gas (U1) are shown in Fig. 5. The color of the front surface of the sample pellet of P1 was changed from gray to black. This implies that a change occurred on the surface. Although it was observed that the grains slightly grew after the reduction from the SEM image, the grains were too small to measure the composition of each grain by EDX. The XRD profiles of the samples before and after the reduction experiment at 800 °C (U1, P1) were shown in Fig. 6. The peaks of TiO₂ and Ni were observed in all diffraction profiles. However, although the color of the surface was changed in the sample of P1, there was no evidence for the reaction of the surface in the XRD profile. Consequently, the surface of the sample pellet P1 was analyzed by GI-XRD and the results are also shown in Fig. 6. The diffraction peaks of Ti₂O₃, which is lower titanium oxide, were observed in the diffraction profile. Thus, we confirmed that Ti₂O₃ formed on the surface of the sample after the reduction by low-temperature hydrogen plasma.

B. Reduction by supercooled monatomic hydrogen

Figure 7 shows the results of XRD analysis before and after the reduction experiments at 1000 °C by atmospheric hydrogen gas (U2) and supercooled monatomic hydrogen (F1 and F2). It was found by XRD that Ti₃O₅ formed after the reduction by supercooled monatomic hydrogen under a filament temperature of 2000 and 2500 °C, whereas Ti₄O₇ formed after the reduction by atmospheric hydrogen gas. This indicates that supercooled monatomic hydrogen is a stronger reductant than atmospheric hydrogen gas. Figure 8 shows backscattered electron images of the samples after reduction. White and gray corresponded to nickel and titanium oxide,

The XRD and GI-XRD profiles of the sample pellet before and after the reduction experiment by low-temperature hydrogen plasma. Symbols show peak positions referred from JCPDS card.

FIG. 5. Photographs and SEM images of the in the reduction experiment by hydrogen plasma. (a) Sample before reduction. (b) Sample reduced at 800 °C by low-temperature hydrogen plasma (P1). (c) Sample reduced at 800 °C by atmospheric hydrogen gas (U1).

FIG. 6. XRD and GI-XRD profiles of the sample pellet before and after the reduction experiment by low-temperature hydrogen plasma.
respectively, by EDX analysis. The grain size is almost identical in all samples, which implies that the temperature of the surface was maintained at around 1000 °C in these three experiments. The concentration of titanium in Ni(ss) was measured by EDX and the results are listed in Table II. The concentration is almost the same in all samples, and independent of the filament temperature. Here, the solubility of titanium is different in Ni(ss) in equilibrium with Ti$_3$O$_5$ or Ti$_4$O$_7$, which are the product phases after the reduction by supercooled monatomic hydrogen or atmospheric hydrogen, respectively. Nevertheless, such a difference of concentration of Ti in Ni(ss) was not observed in EDX analysis. This contradiction is discussed in the next section.

V. DISCUSSION
A. Difference of surface and bulk in the reduction by supercooled monatomic hydrogen

In the experiment of U2, although the concentration of Ti in Ni(ss) by EDX was 1.8 at.%, the titanium oxide identified by XRD was Ti$_4$O$_7$, which must be in equilibrium with pure Ni, as shown in Fig. 2. This contradiction between the experimental results and the phase diagram of Ti–Ni–O system can be explained by the difference of detectable depth between EDX and XRD. The detectable depth of EDX depends on the penetration depth of electron beam, $L_e$, which is represented as follows:

$$L_e = 5.025 \times 10^{-12} \frac{AE_0^{5/3}}{\lambda_{se}pZ^{8/9}}.$$  (3)

Here, $A$, $E_0$, $\lambda_{se}$, $p$, and $Z$ are atomic weight, incident energy of electron beam, density, empirical constant, and atomic number, respectively. Since we measured the concentration of Ti in Ni(ss), we considered the penetration of electron beam into Ni. The $\lambda_{se}$ is 0.182 when $E_0$ is 10 keV. Under this condition, $L_e$ is calculated to be 0.44 μm.

On the other hand, the detectable depth of XRD is estimated from the effective penetration depth of x-rays, $L_X$, which can be calculated using the following equation:

$$L_X = \frac{\sin \theta}{2 \mu} \ln \frac{1}{1 - G}.$$  (4)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Product phase</th>
<th>Concentration of Ti in N(ss) (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (bulk)</td>
<td>Ni, TiO$_2$</td>
<td>Not observed</td>
</tr>
<tr>
<td>P1 (surface)</td>
<td>Ni, Ti$_3$O$_5$, TiO$_2$</td>
<td>Not observed</td>
</tr>
<tr>
<td>F1 (bulk)</td>
<td>Ni, Ti$_3$O$_5$</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>F2 (bulk)</td>
<td>Ni, Ti$_3$O$_5$, Ti$_4$O$_7$</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>U1 (bulk)</td>
<td>Ni, TiO$_2$</td>
<td>Not observed</td>
</tr>
<tr>
<td>U2 (bulk)</td>
<td>Ni, Ti$_4$O$_7$</td>
<td>1.8 ± 0.5</td>
</tr>
</tbody>
</table>

FIG. 8. Backscattered electron images after the reduction experiment by supercooled monatomic hydrogen.
Here, \( \theta \) and \( \mu \) are the incident angle of x-ray and the x-ray linear absorption coefficient, respectively. \( G \) is the ratio of the intensity of the diffracted x-ray from the surface region to the total intensity of the diffracted x-ray. Thus, \( G \) shows the ratio of the information from the surface region of a depth to that from the whole sample in the XRD profile. We regarded the effective penetration depth as the depth giving 99% of the information in XRD profiles. When \( G \) is 0.99, the effective penetration depth of x-rays is 7.4 \( \mu \)m, where \( \theta \) is 10°. This is the case where the effective penetration depth is the shallowest. In fact, when \( \theta \) is 40°, \( \mu \) is calculated to be 27 \( \mu \)m. Thus, we can obtain only the information of the thin layer on the surface region by EDX. Therefore, on the assumption that the titanium oxide formed after the reduction by atmospheric hydrogen gas at 1000 °C is the difference between surface and bulk, as shown in Fig. 9(a), we can then understand why the concentration of Ti in Ni(ss) measured by EDX implies the existence of \( \text{Ti}_3\text{O}_5 \), and \( \text{Ti}_4\text{O}_7 \) was observed by XRD in the sample of U2. Furthermore, we can reasonably assume that the thickness of the \( \text{Ti}_3\text{O}_5 \) layer of the samples after the reduction by supercooled monatomic hydrogen is wider than that by atmospheric hydrogen gas, as shown in Fig. 9. These assumptions might be true because the equilibrium phase with \( \text{H}_2 \) and \( \text{H}_2\text{O} \) (\( p_{\text{H}_2} = 1 \text{ atm}, p_{\text{H}_2\text{O}} = 10^{-4} \text{ atm} \)) is \( \text{Ti}_3\text{O}_5 \) in the chemical potential diagram of Fig. 3(b).

### B. Reduction mechanism of the reduction by nonequilibrium hydrogen gas

Nonequilibrium hydrogen gas, including low-temperature hydrogen plasma and supercooled monatomic hydrogen, is sometimes treated as having a thermodynamically high reduction potential on the assumption of the local equilibrium between water and excited hydrogen.\(^{16}\) We think that the dominant exited hydrogen species is monatomic hydrogen. In Fig. 1(b), we plotted a line for \( RT \ln p_{O_2} \) in equilibrium with \( H \) (monatomic hydrogen) of 1 atm and \( \text{H}_2\text{O} \) of 1 atm. But, considering the results of this study, we have to consider that kinetical reasons lead to such hypothetical high reduction ability in a low-temperature plasma process. The low-temperature hydrogen plasma we used is excited by an electromagnetic field, and supercooled monatomic hydrogen is excited by high temperature. As a result, nonequilibrium hydrogen gas is in a high energy state. This high energy state is recovered by reaction with the surface of the condensed substrate as a release of heat. Since the energy of nonequilibrium hydrogen gas is too high, multiple states of product surface can be allowed. The reacted surface should then move to equilibrium. We call these processes (1) the releasing energy process and (2) the relaxing process. These processes can be illustrated as in Fig. 10. In the releasing energy process, nonequilibrium hydrogen gas reacted with \( \text{TiO}_2 \) accompanied with the removal of oxygen on the surface as water. This reaction leads to a lack of oxygen and formation of \( \text{Ti}_2\text{O}_3 \) or \( \text{Ti}_3\text{O}_5 \) or even more reduced titanium oxides, which are not in equilibrium. In the relaxing process, \( \text{Ti}_2\text{O}_3 \) or \( \text{Ti}_3\text{O}_5 \) then reacts with the water vapor in the gas boundary layer near the sample or with titanium oxide located deeper in the sample. As a result, the equilibrium products \( \text{TiO}_2 \) or \( \text{Ti}_4\text{O}_7 \) are formed. When the relaxing process is slow, the nonequilibrium product remains and it has a higher energy than that in equilibrium. We think this is the case for the reduction by low-temperature plasma at 800 °C. In the case of reduction at 1000 °C, the relaxing process is fast. We see that the product is the same with atmospheric hydrogen gas, although the thickness is different. Actually, we can also see a similar process in plasma nitridation. The reaction rate of plasma nitridation is, as is well known, faster than that of normal nitridation using \( \text{NH}_3 \).\(^{17}\) Using plasma nitridation, many metastable

![FIG. 9. Schematic illustration of the penetration of electron beam and x-ray. Gray layer consists of \( \text{Ti}_3\text{O}_5 \) and Ni. White layer consists of \( \text{Ti}_4\text{O}_7 \) and Ni. (a) Sample reduced at 1000 °C by atmospheric hydrogen gas (U2). (b) Sample reduced at 1000 °C by supercooled monatomic hydrogen (F1, F2).](image-url)
实验结果表明，1000°C下5000个过程的反应速率明显增加。这表明在低温氢气作用下，金属Cu由分子氢还原的反应速率加快，释放过程和放松过程的反应速率分别对应于释放和放松过程。

Kondo et al.19报告了CuO由超冷分子氢还原的反应。

反应过程包括释放过程和放松过程。Kondo et al.19报告了CuO由超冷分子氢还原的反应。

图10展示了没有非平衡氢气作用下TiO2的还原过程。1)释放过程和2)放松过程。

图10. 反应过程的还原没有非平衡氢气作用下TiO2的还原。1)释放过程和2)放松过程。

第10章. 反应过程的还原没有非平衡氢气作用下TiO2的还原。1)释放过程和2)放松过程。

VI. CONCLUSIONS

In this study, we investigated the reduction behaviors of TiO2 in the presence of Ni by atmospheric hydrogen gas and nonequilibrium hydrogen gas, including low-temperature hydrogen plasma and supercooled monatomic hydrogen. Although we could not obtain Ni3Ti as originally planned, we obtained some fundamental knowledge about the reaction mechanism of the reduction by nonequilibrium hydrogen gas. It was clear that nonequilibrium hydrogen gas has a higher reduction potential than atmospheric hydrogen gas. The reduction ability of low-temperature hydrogen plasma, by which TiO2 was reduced to Ti2O3, and that of supercooled monatomic hydrogen, by which TiO2 was reduced to Ti3O5, is only kinetically higher.

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