Reduction of Titanium Oxide in the Presence of Nickel by Supercooled Monatomic Hydrogen

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1. Introduction
   ✓ Titanium
   ✓ Thermodynamics for reduction of titanium oxide by hydrogen

2. Experimental and discussion
   ✓ Reduction of titanium oxide by supercooled monatomic hydrogen
   ✓ Reaction mechanism of molecular hydrogen and monatomic hydrogen

3. Summary
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3. Summary
Titanium

Attractive features
• Excellent specific strength and corrosion resistance.
• Unique properties.
  ex.) Ti-Ni alloy: Shape memory, Superelasticity.

Production process
• Kroll process

\[
\begin{align*}
\text{TiO}_2 + C + \text{Cl}_2 & \rightarrow \text{CO}_2 \quad \text{Chlorination} \\
\text{TiCl}_4 + \text{Mg} & \rightarrow \text{MgCl}_2 \quad \text{Magnesiothermic reduction} \\
\text{MgCl}_2 & \rightarrow \text{Ti} \quad \text{Vacuum distillation}
\end{align*}
\]

Low productivity
High energy consumption

It is desired to develop a new production process.
Reduction of titanium oxide by hydrogen gas

Merit of reduction of titanium oxide by hydrogen gas

- Simplify the production process.

Equilibrium partial pressure of O₂

\[ 2\text{Ti} + \text{O}_2 \rightleftharpoons 2\text{TiO} \]

\[ RT \ln p_{\text{O}_2} = \Delta G° + 2RT \ln \frac{a_{\text{TiO}}}{a_{\text{Ti}}} \]

\[ 2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} \]

\[ RT \ln p_{\text{O}_2} = \Delta G° + 2RT \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \]

Because of \( p_{\text{H}_2\text{O}} > 10^{-4} \text{ atm} \) in gas boundary layer

→ Reduction by hydrogen is difficult.

It might be possible to reduce TiO₂ to metallic state with controlling chemical potentials.
Control chemical potential

The Gibbs energy change for reduction of TiO\(_2\) by hydrogen

\[
\text{TiO}_2 + 2\text{H}_2 = \text{Ti} + 2\text{H}_2\text{O} \quad \Delta G^\circ = +359.1 \text{ kJ mol}^{-1} \quad (1000 \degree \text{C})
\]

\[
\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{Ti}} p_{\text{H}_2\text{O}}^2}{a_{\text{TiO}_2} p_{\text{H}_2}^2}

= \Delta G^\circ + 2.303 RT \left( \log a_{\text{Ti}} + 2 \log p_{\text{H}_2\text{O}} - \log a_{\text{TiO}_2} - 2 \log p_{\text{H}_2} \right)
\]

Previous works

- Hydrogen reduction of TiO\(_2\) in the presence of Pt at 1000 \degree \text{C}.
  \[
  \text{TiO}_2 + \text{Pt} \quad (\text{Ti} : \text{Pt} = 1 : 3) \quad \rightarrow \quad \text{Pt}_3\text{Ti}
  \]
  
  We can obtain metallic titanium with decreased activity in alloy.

  However, the proceed of reaction depended on how much the affinity between titanium and alloying element is.

- Hydrogen reduction of TiO\(_2\) in the presence of Ni at 1000 \degree \text{C}.
  \[
  \text{TiO}_2 + \text{Ni} \quad (\text{Ti} : \text{Ni} = 1 : 3) \quad \rightarrow \quad \text{Ti}_4\text{O}_7 + \text{Ni}
  \]
The Gibbs energy change for reduction of TiO₂ by hydrogen

\[ \text{TiO}_2 + 2\text{H}_2 = \text{Ti} + 2\text{H}_2\text{O} \]

\[ \Delta G^0 = +359.1 \text{ kJ} \cdot \text{mol}^{-1} \text{ (1000 °C)} \]

\[ \Delta G = \Delta G^0 + RT \ln \frac{a_{\text{Ti}} p_{\text{H}_2\text{O}}^2}{a_{\text{TiO}_2} p_{\text{H}_2}^2} \]

\[ = \Delta G^0 + 2.303 RT \left( \log a_{\text{Ti}} + 2 \log p_{\text{H}_2\text{O}} - \log a_{\text{TiO}_2} - 2 \log p_{\text{H}_2} \right) \]

Previous works

- Reduction of TiO₂ at 800 °C by low temperature hydrogen plasma

This result clearly indicates that the partial pressure of hydrogen was hypothetically increased.
Objective in this study

Combining two previous studies
① Alloying with nickel (Decrease log $a_{Ti}$)
② Utilizing nonequilibrium hydrogen (Increase log $p_{H_2}$)

Produce titanium nickel alloy by hydrogen reduction.

Reduction of titanium oxide in the presence of nickel by supercooled monatomic hydrogen was examined.
Today’s contents

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Supercooled monatomic hydrogen

Equilibrium partial pressure of monatomic hydrogen

\[
\text{H}_2 \rightleftharpoons 2\text{H} \quad \log p_H = \frac{1}{2} \left( \log p_{H_2} - \frac{\Delta G^\circ}{2.303 \times RT} \right)
\]

In equilibrium with H\textsubscript{2}, \( p_H = 10^{-2} \text{ atm} \) at 2000 °C

If H generated at 2000 °C is supercooled to 1000 °C with keeping \( p_H \),

Based on the assumption of local equilibrium, partial pressure of supercooled hydrogen gas corresponds to \( 10^8 \text{ atm} \).
Hot-wire method

Molecular hydrogen gas

Equilibrium hydrogen gas including monatomic hydrogen
$T = 2000 \, ^\circ\! C$

Supercooled hydrogen gas including monatomic hydrogen
$T = 1000 \, ^\circ\! C$

Tungsten filament
$T = 2000 \, ^\circ\! C$

Alumina tube

5 cm

Sample pellet
Thickness = 0.2 mm

Nickel boat

Thermocouple
$T = 1000 \, ^\circ\! C$
Experimental Apparatus

Hydrogen generator (Electrolysis of deionized water)

Hydrogen purificatrer (Permeation through palladium)

Infrared radiation thermometer for filament

Mirror

DC source

Thermocouple for sample

H$_2$-H$_2$O $\rightarrow$ H$_2$

H$_2$ $\rightarrow$ Ar

H$_2$ $\rightarrow$ Ar

Tungsten Filament

Alumina tube

Heater

Thermocouple for furnace
Experimental procedure

TiO₂ powder + Ni powder
Mix by ball-milling (8 hours)
Ti : Ni = 1 : 3

Mixed powder
Uniaxis press
(412 MPa, 10 min.)

Sample pellet
Reduction
(H₂ flow rate = 100 ml·min⁻¹
Treatment time = 12 hours)

Reduced sample

Temperature conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample Filament</td>
</tr>
<tr>
<td>F1000</td>
<td>1000 (1000)</td>
</tr>
<tr>
<td>F2000</td>
<td>1000 2000</td>
</tr>
</tbody>
</table>

Analysis
- X-ray diffraction analysis (XRD)
- Field emission scanning electron microscopy (FE-SEM)
- Energy-dispersive X-ray microscopy (EDX)
XRD analysis of reaction products

TiO$_2$ was reduced to lower oxide by supercooled hydrogen gas including monatomic hydrogen than by usual hydrogen gas.
EDX analysis of reaction products

Secondary electron image of F1000

Backscattered electron image of F1000

EDX analysis of reaction products

Ti : 1.8 %  
Ni : 98.2 %  

Nickel phase

Ti : 63.6 %  
Ni : 4.7 %  
O : 31.8 %  

Titanium oxide phase
EDX analysis of reaction products

Backscattered electron image (composition image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti concentration in Ni(ss) [at%]</th>
</tr>
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<tr>
<td>F1000</td>
<td>1.8 ± 0.5</td>
</tr>
<tr>
<td>F2000</td>
<td>1.6 ± 0.4</td>
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</table>

Ti concentration in Ni(ss) was independent of filament temperature. Log $a_{\text{Ti}}$ is not different with each other.
In the result of reduction by usual hydrogen gas (F1000),
- Ti$_4$O$_7$ was observed by XRD
- Ti concentration in Ni(ss) by EDX was 1.8 at%.

Contradiction
Detectable depth in EDX and XRD analysis

Penetration depth of **electron beam** and **X-ray**
- Electron beam into nickel: 0.4 ~ 4 μm.
  - EDX gives **surface** information.
- X-ray into the mixture of titanium oxide and nickel: 20 ~ 200 μm.
  - XRD gives **bulk** information.

**Ti$_3$O$_5$** layer of F1000 might be too thin to be detected in XRD analysis.

Thickness of Ti$_3$O$_5$ layer: F1000 $<<$ F2000
Reaction mechanism

Reduction by molecular hydrogen

Reduction by supercooled monatomic hydrogen

Reduction rate: Monatomic Hydrogen >> Molecular hydrogen

By utilizing supercooled monatomic hydrogen, the reduction ability was *kinetically* enhanced and Ti$_3$O$_5$ layer grew wider.
• We could not obtain metallic titanium by reduction of titanium oxide in the presence of nickel by supercooled monatomic hydrogen. But we obtained the following findings.

<table>
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<tr>
<th>Sample</th>
<th>Temperature [°C]</th>
<th>Detected phase by XRD</th>
<th>Ti concentration in Ni(ss) [at%]</th>
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<td>F1000</td>
<td>1000, 1000</td>
<td>Ti₄O₇, Ni</td>
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<td>F2000</td>
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• In bulk, titanium oxide obtained after reduction by supercooled hydrogen gas including monatomic hydrogen is different from the oxide obtained after reduction by usual hydrogen gas.

• The Ti concentration suggests that the chemical potential of oxygen on pellet surface is independent of filament temperature.

• Reduction rate by supercooled hydrogen gas including monatomic hydrogen is faster than that by usual hydrogen gas. As the result, the detected phase was different in bulk.