A NOVEL RECYCLING PROCESS OF TITANIUM METAL SCRAPs BY USING CHLORIDE WASTES

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1. Introduction
2. Thermodynamic analysis
3. Experimental
4. Experimental results
5. Summary
A NOVEL RECYCLING PROCESS OF TITANIUM METAL SCRAPS BY USING CHLORIDE WASTES

1. Introduction
   • Background
   • Purpose of this study

2. Thermodynamic analysis

3. Experimental

4. Experimental results

5. Summary
1. Introduction

The Kroll process

Chlorination: Ti ore (s) + C (s) + 2 Cl₂ (g) → TiCl₄ (l) + MClₓ (s, g) + CO₂ (g)  
M: Impurity element in the ore

Reduction: TiCl₄ (l) + 2 Mg (s) → Ti (s) + 2 MgCl₂ (l)

Electrolysis: MgCl₂ (l) → Mg (s) + Cl₂ (g)

The essential advantage: High-purity Ti available
The critical disadvantage: Low productivity
1. Introduction

Chlorine cycle in the Kroll process

Although major portion of chlorine in the Kroll process is recycled, chloride wastes are generated in the Kroll process.

The generation of chloride wastes causes not only chlorine loss but also environmental problems.
Current Ti scrap recycle

1) Ti scrap is used for producing ferro-alloys for steel making.

2) In the future, amount of low-purity Ti scrap will increase, and a new recycling process of Ti scrap is required.

http://www.toho-titanium.co.jp/jp/index.html
The purpose of this study

1. Selective chlorination
   - Low-grade Ti ore (FeTiO$_x$)
   - MCI$_x$ (Cl$_2$)
   - Upgraded Ti ore (TiO$_2$)
   - FeCl$_x$ (+ AlCl$_3$)

2. Combined recovery of Ti and Cl
   - Ti scrap
   - FeCl$_x$
   - Fe
   - TiCl$_4$

3. Ti smelting
   - (e.g., Kroll process or PRP process)
   - Ti
   - MCI$_x$ (M = Fe, Al, Si…)

A new Ti smelting process combined with iron removal from low-grade Ti ore by selective chlorination and efficient Ti scrap recovery by utilizing chlorine wastes is investigated with the objective of reducing the production cost and decreasing the environmental burden.
Today’s topic

1. Selective chlorination
   - Low-grade Ti ore (FeTiO_x) → Upgraded Ti ore (TiO_2)

2. Combined recovery of Ti and Cl
   - Ti (s) + FeCl_x (l, g) → TiCl_4 (g) ↑ + Fe (s)

3. Ti smelting
   - Ti metal scrap can be recycled.
   - Chlorine in the chloride wastes can be efficiently recovered.
   - Low-grade Ti ore can be used as the feed material.
   - Cost of waste treatment can be reduced.

(M = Fe, Al, Si…)

(e.g., Kroll process or PRP process)
A NOVEL RECYCLING PROCESS OF TITANIUM METAL SCRAPS BY USING CHLORIDE WASTES

1. Introduction
2. Thermodynamic analysis
3. Experimental
4. Experimental results
5. Summary
2. Thermodynamics analysis

Chemical potential diagram for the Ti-Cl-O system

When $p_{O_2}$ is high, TiCl$_4$ cannot be obtained even under a high $p_{Cl_2}$ atmosphere.

When C or CO is introduced into the system, TiCl$_4$ is generated by the chlorination of TiO$_2$ under a high $p_{Cl_2}$ atmosphere.
Chemical potential diagram for the Fe-Ti-Cl system

Ti present in the Ti scrap can be extracted by iron chlorides.

or

TiCl₄ can be obtained by reacting Ti scraps with chloride wastes.

2. Thermodynamics analysis

Ti (s) + FeClₓ (l, g) → TiCl₄ (g)↑ + Fe (or FeTi, s)
Vapor pressure of some selected chlorides and metals

Temperature, $T / \text{K}$

Vapor pressure, log $p_i$ (atm)

Region suitable for vaporization chlorides

The separation of chlorides and recovery of high-purity TiCl$_4$ are possible by controlling the deposition temperature.

Vapor pressure of some chlorides and metals as a function of reciprocal temperature.
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1. Introduction
2. Thermodynamic analysis
3. Experimental
4. Experimental results
5. Summary
3. Experimental

Experiment apparatus (1)

(Deposits after the experiment) Quartz tube Graphite crucible

Vacuum pump Ar gas

Silicone rubber plug Heating element

Sample mixture e.g., FeCl$_2$ + Ti powder

\[ T = 1100 \, \text{K}; \, t' = 1\, \text{h or 3h}; \, \text{At atmosphere} \]

\[ \text{Ti (s)} + \text{FeCl}_2 (l, g) \rightarrow \text{TiCl}_4 (g) \uparrow + \text{Fe (s)} \]
3. Experimental

Experiment apparatus (2)

(Deposits after the experiment) Quartz tube Graphite crucible

Vacuum pump Ar gas

Heating element

Silicone rubber plug NaOH gas trap Sample mixture e.g., FeCl₂ + Ti powder

NaOH (s) + MClₓ (g) → NaCl (s) + M(OH)ₓ (s)
### Experiment conditions

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Mass of feed materials, $w_i / g$</th>
<th>Mass Ratio $w_{Ti} / w_{FeCl_2}$</th>
<th>Reaction temp., $T / K$</th>
<th>Reaction time, $t' / h$</th>
<th>Atmosphere*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti scraps</td>
<td>FeCl₂ (Powder)</td>
<td>NaOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>0.33</td>
<td>1.90</td>
<td>5.27</td>
<td>5.79</td>
<td>Ar</td>
</tr>
<tr>
<td>CB</td>
<td>0.30</td>
<td>1.75</td>
<td>3.18</td>
<td>5.79</td>
<td>Ar</td>
</tr>
<tr>
<td>CC</td>
<td>0.32</td>
<td>1.72</td>
<td>5.36</td>
<td>1100</td>
<td>Ar</td>
</tr>
<tr>
<td>CD</td>
<td>0.49</td>
<td>2.76</td>
<td>3.25</td>
<td>1100</td>
<td>Ar</td>
</tr>
<tr>
<td>CE</td>
<td>0.51</td>
<td>2.86</td>
<td>5.47</td>
<td>1100</td>
<td>Ar</td>
</tr>
<tr>
<td>CF</td>
<td>0.50</td>
<td>3.17</td>
<td>5.38</td>
<td>1100</td>
<td>Ar</td>
</tr>
</tbody>
</table>

a: Ti powder was used in this experiment.
b: Ti shot was used in this experiment.
c: Ti turning was used in this experiment.

*: Reduced atmosphere (0.2 atm at room temperature).

Ti (s) + 2 FeCl₂ (l, g) = TiCl₄ (g) + 2 Fe (s)

Stoichiometric amount of Ti to FeCl₂ is 1:5.29.
A NOVEL RECYCLING PROCESS OF TITANIUM METAL SCRAPs BY USING CHLORIDE WASTES

1. Introduction
2. Thermodynamic analysis
3. Experimental
4. Experimental results
   • XRD, XRF, ICP-AES, and potentiometric titration method
5. Summary
4. Experimental results

The distribution of the temperature

Distribution of temperature in the horizontal furnace.

Assembled quartz tube after experiment.
4. Experimental results

Observation

Assembled quartz tube after experiment.

The image of the obtained residue and deposit after experiment.

Silicone plug
Solid (White)
Flake (Brown)
Residue (Black)

Silicone plug after experiment
Deposit on the surface of the NaOH gas trap
Deposit inside the quartz tube
Residue in the graphite crucible

Melting point of FeCl₂: 950 K @ 1 atm
Melting point of TiCl₄: 408 K @ 1 atm
## Ti powder without NaOH gas trap: Composition

Analytical results of the samples before and after heating, and the deposits obtained on the surface of silicone plug and inside the quartz tube after heating.

<table>
<thead>
<tr>
<th>Exp. CC</th>
<th>Concentration of element $i$, $C_i$ (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Initial sample before heating</td>
<td>15.7$^a$</td>
</tr>
<tr>
<td>Residue in the graphite crucible</td>
<td>8.95$^b$</td>
</tr>
<tr>
<td>Deposit inside the quartz tube</td>
<td>0.33$^c$</td>
</tr>
<tr>
<td>Deposit on the surface of silicone plug</td>
<td>(16.7$^b$)</td>
</tr>
</tbody>
</table>

The value excludes carbon and gasous elements except Cl.

- a: Calculated.
- b: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
- c: Determined by X-ray fluorescence analysis (XRF).
- d: Determined by potentiometric titration method.

$C_{Ti}$: 15.7% $\rightarrow$ 8.95%.
$C_{Fe}$: 37.2% $\rightarrow$ 91.1%.
$TiCl_x$ ($TiCl_4$) obtained.

The silicone plug was damaged due to the reaction with $TiCl_4$. 

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4. Experimental results
4. Experimental results

**Ti powder without NaOH gas trap: XRD**

Before experiment

![XRD pattern before experiment](image)

After experiment

![XRD pattern after experiment](image)

XRD patterns of the sample before experiment (a) and the residue after experiment (b) (Exp. CC)

**Fe was generated at heating zone.**

\[ \text{Ti} (s) + \text{FeCl}_2 (l, g) \rightarrow \text{TiCl}_4 (g) \uparrow + \text{Fe} (s) \]
4. Experimental results

**Discussion (1)**

Chemical potential diagram for the Fe-Ti-Cl system at 1100 K

The obtained experimental results are in good agreement with the thermodynamic analysis.

\[
\text{Ti} (s) + \text{FeCl}_2 (l, g) \quad \rightarrow \quad \text{TiCl}_4 (g) \uparrow \quad + \quad \text{Fe} (s)
\]

Reaction proceeded at point “A” under Fe(s) / FeCl₂(s) / TiCl₄(g) equilibrium.

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Institute of Industrial Science, The University of Tokyo

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Ti in Ti scraps was recovered by FeCl\textsubscript{2} as the form of TiCl\textsubscript{4}, but the silicone plug was damaged due to the reaction with the TiCl\textsubscript{4}.

NaOH was introduced as a gas trap for recovering TiCl\textsubscript{4}.
## Ti powder: Composition

Analytical results of the samples before and after heating, and the deposits obtained on the surface of the NaOH gas trap and inside the quartz tube after heating.

<table>
<thead>
<tr>
<th>Exp. CB</th>
<th>Concentration of element $i$, $C_i$ (mass%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Initial sample before heating</td>
<td>$14.6^a$</td>
</tr>
<tr>
<td>Residue in the graphite crucible</td>
<td>$4.90^b$</td>
</tr>
<tr>
<td>Deposit inside the quartz tube</td>
<td>$2.71^c$</td>
</tr>
<tr>
<td>Deposit on the surface of the NaOH gas trap</td>
<td>$(16.7^b)$</td>
</tr>
</tbody>
</table>

The value excludes carbon and gasous elements except Cl.

- $a$: Calculated.
- $b$: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
- $c$: Determined by X-ray fluorescence analysis (XRF).
- $d$: Determined by potentiometric titration method.

$C_{Ti}: 14.6\% \rightarrow 4.90\%.$

$C_{Fe}: 37.5\% \rightarrow 95.1\%.$

There was no damage on the silicone plug.

$\rightarrow$ The obtained TiCl$_4$ was recovered by NaOH successfully.
4. Experimental results

XRD patterns of the sample before experiment (a) and the residue after experiment (b) (Exp. CB)

Fe was generated at heating zone.

\[
\text{Ti} \ (s) + \text{FeCl}_2 \ (l, g) \rightarrow \text{TiCl}_4 \ (g) + \text{Fe} \ (s)
\]
### Ti granule and turning: Composition

<table>
<thead>
<tr>
<th>Exp. CD</th>
<th>Concentration of element $i$, $C_i$ (mass%)</th>
<th>Ti</th>
<th>Fe</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Feed material: Ti granule)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial sample before heating</td>
<td>15.1$^a$</td>
<td>37.4$^a$</td>
<td>47.5$^a$</td>
<td></td>
</tr>
<tr>
<td>Residue in the graphite crucible</td>
<td>62.8$^b$</td>
<td>37.2$^b$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Deposit inside the quartz tube</td>
<td>0.10$^b$</td>
<td>49.7$^b$</td>
<td>50.2$^c$</td>
<td></td>
</tr>
<tr>
<td>Deposit on the surface of NaOH gas trap</td>
<td>0.15$^b$</td>
<td>0.38$^b$</td>
<td>99.5$^c$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exp. CF</th>
<th>Concentration of element $i$, $C_i$ (mass%)$^d$</th>
<th>Ti</th>
<th>Fe</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Feed material: Ti turning)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial sample before heating</td>
<td>13.6$^a$</td>
<td>38.1$^a$</td>
<td>48.3$^a$</td>
<td></td>
</tr>
<tr>
<td>Residue in the graphite crucible</td>
<td>29.1$^d$</td>
<td>64.7$^d$</td>
<td>6.18$^d$</td>
<td></td>
</tr>
<tr>
<td>Deposit inside the quartz tube</td>
<td>0.06$^d$</td>
<td>50.3$^d$</td>
<td>49.6$^d$</td>
<td></td>
</tr>
<tr>
<td>Deposit on the surface of the NaOH gas trap</td>
<td>(0.04$^d$)</td>
<td>(1.29$^d$)</td>
<td>(98.7$^d$)</td>
<td></td>
</tr>
</tbody>
</table>

The value excludes carbon and gasous elements except Cl.

a: Calculated.
b: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
c: Determined by the potentiometric titration method.
d: Determined by X-ray fluorescence analysis (XRF).

**Black coat was formed on the surface of the residue.**

**The residue was magnetic material.**

**Fe element presents in the residue after heating.**
### 4. Experimental results

#### Mass balance

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Form of Ti scraps</th>
<th>Mass of feed materials, $w_i / \text{g}$</th>
<th>Mass of the obtained sample, $w / \text{g}$</th>
<th>Concentration of Ti (mass%)</th>
<th>Recovery Ratio of Ti, $R (%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA$^b$</td>
<td>Powder</td>
<td>0.33 Ti scraps 1.90 FeCl$_2$ (Powder)</td>
<td>0.56</td>
<td>1.89</td>
<td>97</td>
</tr>
<tr>
<td>CB$^b$</td>
<td>Powder</td>
<td>0.30 Ti scraps 1.75 FeCl$_2$ (Powder)</td>
<td>0.72</td>
<td>4.90</td>
<td>88</td>
</tr>
<tr>
<td>CC$^b$</td>
<td>Powder</td>
<td>0.32 Ti scraps 1.72 FeCl$_2$ (Powder)</td>
<td>0.66</td>
<td>8.95</td>
<td>82</td>
</tr>
<tr>
<td>CD$^c$</td>
<td>Granule</td>
<td>0.49 Ti scraps 2.76 FeCl$_2$ (Powder)</td>
<td>0.73</td>
<td>62.8</td>
<td>6.8</td>
</tr>
<tr>
<td>CE$^c$</td>
<td>Granule</td>
<td>0.51 Ti scraps 2.86 FeCl$_2$ (Powder)</td>
<td>0.62</td>
<td>45.3</td>
<td>45</td>
</tr>
<tr>
<td>CF$^d$</td>
<td>Turning</td>
<td>0.50 Ti scraps 3.17 FeCl$_2$ (Powder)</td>
<td>0.62</td>
<td>29.1</td>
<td>64</td>
</tr>
</tbody>
</table>

a: Experiment date.
b: Ti powder was used in this experiment.
c: Ti granules was used in this experiment.
d: Ti turning was used in this experiment.

When Ti powder was used as the feed material, recovery ratio of Ti was obviously higher than those when Ti granule or turning was used.

The reaction speed was affected by the morphology of the Ti scraps.
5. Summary

A NOVEL RECYCLING PROCESS OF TITANIUM METAL SCRAPS BY USING CHLORIDE WASTES

Summary

1. Ti in Ti scraps was extracted by chloride wastes as the form of TiCl$_4$.

2. Fe was generated at heating zone.

3. The obtained experimental results are in good agreement with the thermodynamic analysis:

$$\text{Ti} \,(s) + \text{FeCl}_2 \,(l, g) \rightarrow \text{TiCl}_4 \,(g) + \text{Fe} \,(s)$$

4. The recovery ratio of Ti and Cl as well as the reaction speed were largely dependent on the morphology of the Ti scraps: Ti scraps in the form of powder is easier to be recycled by FeCl$_2$ than Ti granule or Ti turning.
The purpose of this study

A new Ti smelting process combined with iron removal from low-grade Ti ore by selective chlorination and efficient Ti scrap recovery by utilizing chlorine wastes is investigated with the objective of reducing the production cost and decreasing the environmental burden.
For Questions and Answers
Iron removal from low-grade Ti ore by selective chlorination

Analytical results of the obtained sample after selective chlorination.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Concentration of element $i$, $C_i$ (mass%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Ti ore$^b$</td>
<td>0.1</td>
</tr>
<tr>
<td>SCD</td>
<td>n.d.</td>
</tr>
<tr>
<td>SCO</td>
<td>n.d.</td>
</tr>
<tr>
<td>SCP</td>
<td>n.d.</td>
</tr>
<tr>
<td>SCS</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

$^a$: Determined by X-ray fluorescence analysis (XRF), the value excludes carbon and gaseous elements,

n.d. = not detected (below 0.1 %)

$^b$: Natural ilmenite ore produced in Vietnam.

$^c$: $R = 100 \times \{1 - (C_{Fe, after} / C_{Ti, after}) / (C_{Fe, before} / C_{Ti, before})\}$.

After experiment: $C_{Fe}$: 51.3% $\rightarrow$ 3.2%

Fe was removed from Ti ore successfully.
Prefrom reduction process (PRP)

- **Mixing**
  - Ti ore
  - Flux
  - Binder
  - Slurry

- **Preform fabrication**
  - Rutile + CaCl₂ + Binder
  - \( T: \text{Room temp.}, t': 6 \text{ h} \)
  - e.g. 40mm × 20mm × 8mm

- **Feed preform**
  - Calcination/iron removal
  - \( T: 1273 \text{ K}, t': 1 \sim 2 \text{ h} \)

- **Sintered feed preform**
  - Reduction
  - Calcium vapor
  - \( T: 1273 \text{ K}, t': 6 \sim 10 \text{ h} \)

- **Reduced preform**
  - Leaching
  - Waste solution
  - Ti powder
  - \( 0.8 \sim 1.4 \text{ mass} \% \ Fe \)
  - 90% Fe removal
  - \( \sim 0.13 \text{ mass} \% \ Fe \)
  - 98 mass% up purity
  - 0.14 mass% Fe
  - 88% yield

- **Calcination/iron removal**
  - \( FeCl_x \)
  - \( TiO_2 \text{ feed in flux} \)

- **Sintered feed preform**
  - Ti ore + flux

- **Ti ore: Rutile**
  - Flux: CaCl₂
  - Binder: Collodion

- **Leaching**
  - \( 50\% \text{ CH}_3\text{COOH aq.}, t': 6 \text{ h} \)
  - 20% HCl aq., \( t': 1 \text{ h} \)

- **Vacuum drying**
  - Powder

- **90% Fe removal**

- **88% yield**
Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

Ti ore → Flux → Binder → Mixing → Slurry

Rutile + CaCl₂ + Binder

- T: Room temp.; t': 6 hr (e.g., 40mm × 20mm × 8mm)

Preform fabrication

Feed preform → Calcination/iron removal

- T: 1273 K; t': 1 hr ~ 2hr

Sintered feed preform

Calcination/iron removal → FeClₓ

Reduction

Reduced preform

Leaching

- T: RT
- 50% CH₃COOH aq., t: 6 hr
- 20% HCl aq., t': 1 hr

Vacuum drying

Powder

- 0.8~1.4 mass % Fe
- 90% Fe removal
- ~0.13 mass % Fe

98 mass % up purity
- 0.14 mass % Fe
- 88% yield
Titanium (Ti) ?

1. Light and high-strength
2. Corrosion resistance
3. Biocompatibility
4. Special alloy (Shape memory alloy, Superelastic alloy…)
5. Ninth most abundant element
1791 Gregor: Discovery of titanium element

1795 Klaproth: Denominated as “Titanium”

1887 Nilson, Petterson: Reduction of TiCl₄ by Na

1910 Hunter: Reduction of TiCl₄ by Na

1925 van Arkel, DeBore: Thermal dissociation of TiCl₄

1940 Kroll: Reduction of TiCl₄ by Mg

Current titanium production process based on the Kroll process.
History of Titanium

1791
First discovered by William Gregor, a clergyman and amateur geologist in Cornwall, England

1795
Klaproth, a German chemist, gave the name titanium to an element re-discovered in Rutile ore.

1887
Nilson and Pettersson produced metallic titanium containing large amounts of impurities

1910
M. A. Hunter produced titanium with 99.9% purity by the sodiothermic reduction of TiCl₄ in a steel vessel.

(119 years after the discovery of the element)

1946
W. Kroll developed a commercial process for the production of titanium: Magnesiothermic reduction of TiCl₄.

Titanium was not purified until 1910, and was not produced commercially until the early 1950s.
Titanium is the 10\textsuperscript{th} most abundant element in the earth’s crust

<table>
<thead>
<tr>
<th>Rank</th>
<th>Element</th>
<th>Clark #.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^8$O</td>
<td>49.50</td>
</tr>
<tr>
<td>2</td>
<td>$^{14}$Si</td>
<td>25.80</td>
</tr>
<tr>
<td>3</td>
<td>$^{13}$Al</td>
<td>7.56</td>
</tr>
<tr>
<td>4</td>
<td>$^{26}$Fe</td>
<td>4.70</td>
</tr>
<tr>
<td>5</td>
<td>$^{20}$Ca</td>
<td>3.39</td>
</tr>
<tr>
<td>6</td>
<td>$^{11}$Na</td>
<td>2.63</td>
</tr>
<tr>
<td>7</td>
<td>$^{19}$K</td>
<td>2.40</td>
</tr>
<tr>
<td>8</td>
<td>$^{12}$Mg</td>
<td>1.93</td>
</tr>
<tr>
<td>9</td>
<td>$^{1}$H</td>
<td>0.87</td>
</tr>
<tr>
<td>10</td>
<td>$^{22}$Ti</td>
<td>0.46</td>
</tr>
<tr>
<td>11</td>
<td>$^{17}$Cl</td>
<td>0.19</td>
</tr>
<tr>
<td>12</td>
<td>$^{25}$Mn</td>
<td>0.09</td>
</tr>
<tr>
<td>13</td>
<td>$^{15}$P</td>
<td>0.08</td>
</tr>
<tr>
<td>14</td>
<td>$^{6}$C</td>
<td>0.08</td>
</tr>
<tr>
<td>15</td>
<td>$^{16}$S</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The tenth most abundant element

<table>
<thead>
<tr>
<th>Rank</th>
<th>Element</th>
<th>Clark #.</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>$^{7}$N</td>
<td>0.03</td>
</tr>
<tr>
<td>17</td>
<td>$^{9}$F</td>
<td>0.03</td>
</tr>
<tr>
<td>18</td>
<td>$^{39}$Rb</td>
<td>0.03</td>
</tr>
<tr>
<td>19</td>
<td>$^{56}$Ba</td>
<td>0.02</td>
</tr>
<tr>
<td>20</td>
<td>$^{40}$Zr</td>
<td>0.02</td>
</tr>
<tr>
<td>21</td>
<td>$^{24}$Cr</td>
<td>0.02</td>
</tr>
<tr>
<td>22</td>
<td>$^{38}$Sr</td>
<td>0.02</td>
</tr>
<tr>
<td>23</td>
<td>$^{23}$V</td>
<td>0.02</td>
</tr>
<tr>
<td>24</td>
<td>$^{28}$Ni</td>
<td>0.01</td>
</tr>
<tr>
<td>25</td>
<td>$^{29}$Cu</td>
<td>0.01</td>
</tr>
<tr>
<td>26</td>
<td>$^{74}$W</td>
<td>$6 \times 10^{-3}$</td>
</tr>
<tr>
<td>27</td>
<td>$^{3}$Li</td>
<td>$6 \times 10^{-3}$</td>
</tr>
<tr>
<td>28</td>
<td>$^{58}$Ce</td>
<td>$4.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>29</td>
<td>$^{27}$Co</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>30</td>
<td>$^{50}$Sn</td>
<td>$4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Exhausting element...
### Comparison of Ti with common metal

<table>
<thead>
<tr>
<th>Metal</th>
<th>Iron</th>
<th>Aluminum</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Fe</td>
<td>Al</td>
<td>Ti</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1536</td>
<td>660</td>
<td>1680</td>
</tr>
<tr>
<td>Density (g/cm³@25 °C)</td>
<td>7.9</td>
<td>2.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Specific strength [(kgf/mm²)/(g/cm³)]</td>
<td>4.1(Pure)</td>
<td>2.2(Pure)</td>
<td>5.1(Pure)</td>
</tr>
<tr>
<td></td>
<td>6.7(SUS304)</td>
<td>8.9(0.5Mg0.5Si)</td>
<td>24.6(6Al4V)</td>
</tr>
<tr>
<td>Clarke No.</td>
<td>4</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Price (¥/kg)</td>
<td>50</td>
<td>200~600</td>
<td>1300~3000</td>
</tr>
<tr>
<td>Production volume (t/world@2004)</td>
<td>10.5 x 10⁸</td>
<td>2.4 x 10⁷</td>
<td>7.7 x 10⁴</td>
</tr>
</tbody>
</table>

Although Ti is the **ninth most abundant element** in Earth’s crust, its production volume is very small.
Current status of Ti production

(a) Production of Ti sponge in the world (2004)

- USA: 8 kt
- China: 5 kt
- Russia: 27 kt
- Kazakhstan: 13 kt
- Japan: 23.5 kt (31% share)
- Total: 76.5 kt

(b) Transition of production volume of Ti mill products in Japan

Japan has about 30% world market share, and its titanium industry is growing steadily.
Transition of production volume of titanium sponge and mill products in China.
Ref(1): China Titanium Association (Courtesy of Mr. Akiyama, JTS)
Ref(2): China Titanium Association (H. Z., Private communication)
Current status of Ti production

(a) Production of Ti sponge in the world (2004)

- China: 5 kt (7% share)
- USA: 8 kt
- Russia: 27 kt
- Kazakhstan: 13 kt
- Japan: 23.5 kt
- Total: 76.5 kt

(b) Transition of production volume of Ti mill products in Japan

Although China has only about 7% world market share, its titanium industry is growing sharply in recent years.

Ref (1): China Titanium Association (Courtesy of Mr. Akiyama, JTS)
Ref (2): China Titanium Association (H. Z., Private communication)
Shipments of titanium mill product in various field’s application in China (2004).
The Kroll process

Ti feed (TiO₂)  Reductant (C)  Chlorine (Cl₂)

Carbo-chlorination

Crude TiCl₄  CO₂  FeClₓ, AlCl₃

Distillation  H₂S etc.

Pure TiCl₄  Other compounds  Mg

Reduction

Sponge Ti + MgCl₂ + Mg

Vacuum distillation

Sponge Ti  MgCl₂ + Mg

Crushing / Melting

Ti Ingot

Electrolysis

MgCl₂

TiCl₄ (g) + 2 Mg (l) → Ti (s) + 2 MgCl₂ (l)

The essential advantage: High-purity titanium available.
The Kroll process

Chlorination: $\text{Ti ore} \ (s) + \text{C} \ (s) + 2 \text{Cl}_2 \ (g) \rightarrow \text{TiCl}_4 \ (l) + M\text{Cl}_x \ (s, g) + \text{CO}_2 \ (g)$

Reduction: $\text{TiCl}_4 \ (l) + 2 \text{Mg} \ (s) \rightarrow \text{Ti} \ (s) + 2 \text{MgCl}_2 \ (l)$

Electrolysis: $\text{MgCl}_2 \ (l) \rightarrow \text{Mg} \ (s) + \text{Cl}_2 \ (g)$

The essential advantage: High-purity titanium available.
Advantages of the Kroll process

Reduction: $\text{TiCl}_4 \, (l) + 2 \, \text{Mg} \, (s) \rightarrow \text{Ti} \, (s) + 2 \, \text{MgCl}_2 \, (l)$

◎ High-purity Ti can be obtained.
◎ The separation of Ti and salt is easy.
○ Chlorine and Mg can be efficiently recycled in the system.
○ MgCl$_2$ electrolysis with high efficiency can be utilized.
○ Reduction process and electrolysis process are separated completely.
Problems of the Kroll process

The critical disadvantage of the Kroll process is its “low productivity” because of the following factors:

× Complex, labor consuming, and multi-step batch type
× Slow production speed (~ 1 ton / day · reactor)
× Huge heat generated during the reduction step
  → It takes time for removing MgCl₂ and cooling the reactor.
× Contamination of iron from reaction vessel unavoidable
× Chloride wastes generated although expensive titanium concentrates with high TiO₂ was used
  → The usage of expensive titanium concentrates causes high Ti production cost.
  → The generation of chloride wastes causes chlorine loss in the process.
  → Chloride wastes causes environmental burden.
  → Disposal cost of chloride wastes is high.
Direct reduction of TiO₂ (1)

(a) FFC process (Fray et al.)

Electrolysis
Cathode: TiO₂ + 4e⁻ → Ti + 2O²⁻ \hspace{1cm} (a1)
Anode: C + x O²⁻ → COₓ + 2x e⁻ \hspace{1cm} (a2)

(b) OS process (Ono & Suzuki)

TiO₂ + 2Ca → Ti + 2O²⁻ + Ca²⁺ \hspace{1cm} (b1)
Electrolysis
Cathode: Ca²⁺ + 2e⁻ → Ca \hspace{1cm} (b2)
Anode: C + x O²⁻ → COₓ + 2x e⁻ \hspace{1cm} (b3)

Several new smelting processes for producing Ti by direct reduction of TiO₂ are under investigation recently.
Direct reduction of TiO$_2$ (2)

(c) EMR/MSE process (Okabe et al.)

\[
\text{Cathode: } \text{TiO}_2 + 4e^- \rightarrow \text{Ti} + 2\text{O}^{2-} \quad (c1)
\]
\[
\text{Anode: } 2\text{Ca} \rightarrow 2\text{Ca}^{2+} + 4e^- \quad (c2)
\]

\text{Electrolysis}

\[
\text{Cathode: } \text{Ca}^{2+} + 2e^- \rightarrow \text{Ca} \quad (c3)
\]
\[
\text{Anode: } \text{C} + x \text{O}^{2-} \rightarrow \text{CO}_x + 2x \text{e}^- \quad (c4)
\]

\text{Overall reaction}

\[
\text{TiO}_2 + \text{C} \rightarrow \text{Ti} + \text{CO}_2 \quad (c5)
\]

Problems:

- The control of the contamination from the system is difficult;
- The process for producing high purity TiO$_2$ feed is high cost;
- The electric efficiency is low;
- The reduction speed is slow;
- The separation of salt and Ti is difficult;
- A large amount of molten salt is used.
Direct reduction of TiO$_2$ (3)

(d) Preform reduction process (PRP)

Calciothermic reduction

\[ \text{TiO}_2 + 2\text{Ca} \rightarrow \text{Ti} + 2\text{CaO} \]

Feed preform
(TiO$_2$ feed + flux)

Reductant vapor

Reductant
(R = Ca or Ca-X alloy)

PRP will be stated in the Chapter 5.
Features of reductant and feed materials in metallothermic reduction process.

<table>
<thead>
<tr>
<th></th>
<th>TiCl$_4$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>☄️ Possible to remove Mg and MgCl$_2$ by distillation.</td>
<td>× Impossible to remove oxygen</td>
</tr>
<tr>
<td></td>
<td>Possible to efficiently electrolysis MgCl$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Easy to control purity (strong contamination of carbon)</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>☀️ Difficult to remove Na</td>
<td>× Impossible to remove oxygen</td>
</tr>
<tr>
<td></td>
<td>Difficult to control the temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Easy to purity control (strong resistance to Ni contamination)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>△ High energy loss</td>
<td>☐ Difficult to purity control</td>
</tr>
<tr>
<td></td>
<td>Difficult to remove Ca or CaCl$_2$</td>
<td>Difficult to remove Ca or CaCl$_2$</td>
</tr>
<tr>
<td></td>
<td>Cost of the reductant production</td>
<td>Cost of the reductant production</td>
</tr>
</tbody>
</table>

↑ Process with strong resistance to Oxygen
## Comparison of various processes

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kroll</td>
<td>◎High purity titanium available</td>
<td>×Complicated process</td>
</tr>
<tr>
<td></td>
<td>◎Easy metal / salt separation</td>
<td>×Slow production speed</td>
</tr>
<tr>
<td></td>
<td>○Established chlorine circulation</td>
<td>×Batch type process</td>
</tr>
<tr>
<td></td>
<td>○Utilizes efficient Mg electrolysis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>○Reduction and electrolysis operation can be carried out independently</td>
<td></td>
</tr>
<tr>
<td>FFC</td>
<td>◎Simple process</td>
<td>×Difficult metal / salt separation</td>
</tr>
<tr>
<td></td>
<td>○Semi-continuous process</td>
<td>×Reduction and electrolysis have to be carried out simultaneously</td>
</tr>
<tr>
<td></td>
<td></td>
<td>△Sensitive to carbon and iron contamination</td>
</tr>
<tr>
<td>OS</td>
<td>◎Simple process</td>
<td>×Difficult metal / salt separation</td>
</tr>
<tr>
<td></td>
<td>○Semi-continuous process</td>
<td>△Sensitive to carbon and iron contamination</td>
</tr>
<tr>
<td></td>
<td></td>
<td>△Low current efficiency</td>
</tr>
<tr>
<td>EMR / MSE</td>
<td>◎Resistant to iron and carbon contamination</td>
<td>×Difficult metal / salt separation when oxide system</td>
</tr>
<tr>
<td></td>
<td>○Semi-continuous process</td>
<td>×Complicated cell structure</td>
</tr>
<tr>
<td></td>
<td>○Reduction and electrolysis operation can be carried out independently</td>
<td>△Complicated process</td>
</tr>
<tr>
<td>FFC</td>
<td>◎Effective control of purity and morphology</td>
<td>×Difficult recovery of reductant</td>
</tr>
<tr>
<td></td>
<td>◎Flexible scalability</td>
<td>×Environmental burden by leaching</td>
</tr>
<tr>
<td></td>
<td>◎Resistant to contamination</td>
<td></td>
</tr>
<tr>
<td></td>
<td>○Small amount of fluxes necessary</td>
<td></td>
</tr>
<tr>
<td>Kroll</td>
<td>◎High speed reduction process</td>
<td>×Difficulty of TiCl₂ handling</td>
</tr>
<tr>
<td></td>
<td>○Semi-continuous process</td>
<td>△Multiple reduction process</td>
</tr>
<tr>
<td></td>
<td>○Titanium scrap enable</td>
<td></td>
</tr>
<tr>
<td></td>
<td>○Facilities for Kroll process can be utilized</td>
<td></td>
</tr>
</tbody>
</table>
The concept of the combined recovery of Ti scraps and chloride wastes

Resource scraps

Titanium scraps

Valuable material

Titanium feed

(TiCl₄)

Costly waste disposal

Chloride wastes

(FeClₓ)

Cheap wastes disposal

Iron scraps

(Chlorine free wastes)

Titanium in the scraps and chlorine in the wastes are recovered simultaneously.

Therefore, not only is chlorine loss in the Kroll process reduced but also waste treatment cost can be reduced.
Upgrading Ti ore for minimizing chloride wastes

When low-grade ore is used, a large amount of chloride wastes (e.g., FeCl$_x$) are generated in the Kroll process.

- Disposal cost of chloride wastes
- Environmental issues
- Causes chlorine loss in the process

Currently expensive upgraded ilmenite ore (UGI) is used for reducing chloride waste and environmental burden.
Becher process.

**Institute of Industrial Science, The University of Tokyo**


**Becher process.**

- **Ilmenite** → **Coal (low ash)** → **Air**
  - Reduction (in kiln)
  - **Reduced ore**
  - **Gas + particle** → **Particle**
  - **Screen**
    - **-1 mm**
    - **+1 mm**
  - **Mag. separator** → **Waste (Non. mag.)**
  - **Reduced ilmenite**
  - **NH₄Cl** → **Air**
  - **Leaching**
    - **TiO₂**
    - **H₂SO₄ aq.**
    - **Iron oxide + Sol.**
    - **Acid Leaching**
    - **TiO₂**
    - **Filtering / Drying**
    - **TiO₂ (Synthetic rutile)**
      - TiO₂ 92~93%; TiFe 2.0~3.5%
Benilite process.

Ilmenite → Reduction (in kiln) → Reduced ore → Leaching (in digestor) → Filtration → Calcination

- Reductant (Heavy oil etc.)
- $\text{Fe}^{2+} / \text{TFe} = 80$~$95\%$

- $145^\circ\text{C}$ (2.5 kg/cm$^2$) *4 hr *2 step

Leached ilmenite → Water → Spray acid → Fuel

- HCl vapor
- HCl aq.

Filtration

- TiO$_2$
- Sol.

Roasting

- Iron oxide (90% purity)
- HCl

Absorber

- HCl aq.

Calcination

- TiO$_2$ (Synthetic rutile) 95% TiO$_2$
- 1% TiFe

HCl aq.
Metallothermic reduction process for producing Ti powder

(a) Conventional Hunter Process

- High purity & homogeneous powder can be produced
- Suitable for uniform reduction
- High cost process
- Batch type process
- Large amount of salt is used, and large amount of waste solution generated
- Uses highly reactive reductant

(b) Conventional Metallothermic Reduction

- Simple and low cost process
- Flexible scalability
- Difficult morphology control
- Sensitive to contamination from reaction container
The concept of this study

A new Ti smelting process combined with iron removal from low-grade Ti ore by selective chlorination and efficient chlorine recovery by utilizing Ti scraps is investigated with the objective of reducing the production cost and decreasing the environmental burden.
The objective of this study

1. Iron removal from low-grade Ti ore by selective chlorination method using metal chlorides as the resource of chlorine (Chapter 3)

2. Chlorine recovery by utilizing Ti scraps (Chapter 4)

3. Ti powder production directly from Ti ore by calciothermic reduction (PRP, Chapter 5)

4. Thermodynamic analysis on the abovementioned processes (Chapter 2)
Table  Gibb's energy change of formation and reaction in this study.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Gibbs energy change, $\Delta G^\circ_f$ or $\Delta G^\circ_r$ (kJ/mol) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TiO}_2 (s) + \text{FeO} (s) = \text{FeTiO}_3 (s)$</td>
<td>900 K: -12.74, 1000 K: -11.87, 1100 K: -10.99, 1200 K: -10.10, 1300 K: -9.21</td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + \text{CaO} (s) = \text{CaTiO}_3 (s)$</td>
<td>900 K: -86.44, 1000 K: -87.24, 1100 K: -88.06, 1200 K: -88.89, 1300 K: -89.74</td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + \text{Fe}_2\text{O}_3 (s) = \text{Fe}_2\text{TiO}_5 (s)$</td>
<td></td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + \text{MgO} (s) = \text{MgTiO}_3 (s)$</td>
<td>900 K: -24.29, 1000 K: -24.13, 1100 K: -24.01, 1200 K: -23.94, 1300 K: -23.90</td>
</tr>
<tr>
<td>MgCl$_2$ as chlorine source</td>
<td></td>
</tr>
<tr>
<td>$\text{FeO} (s) + \text{MgCl}_2 (s,l) = \text{FeCl}_2 (l,g) + \text{MgO} (s)$</td>
<td>900 K: -22.39, 1000 K: -22.97, 1100 K: -22.05, 1200 K: -21.14, 1300 K: -18.83</td>
</tr>
<tr>
<td>$\text{FeTiO}_3 (s) + \text{MgCl}_2 (s,l) = \text{FeCl}_2 (l,g) + \text{TiO}_2 (s) + \text{MgO} (s)$</td>
<td>900 K: -9.65, 1000 K: -11.10, 1100 K: -11.06, 1200 K: -11.04, 1300 K: -9.62</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3 (s) + 3\text{MgCl}_2 (g) = 2\text{FeCl}_2 (g) + 3\text{MgO} (s)$</td>
<td></td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + 2\text{MgCl}_2 (s,l) = \text{TiCl}_4 (g) + 2\text{MgO} (s)$</td>
<td>900 K: 112.53, 1000 K: 99.25, 1100 K: 94.02, 1200 K: 89.23, 1300 K: 84.84</td>
</tr>
<tr>
<td>MgCl$_2$ (s,l) + H$_2$O(g) = MgO(s) + 2HCl (g)</td>
<td>900 K: -8.67, 1000 K: -19.20, 1100 K: -25.77, 1200 K: -32.16, 1300 K: -38.41</td>
</tr>
<tr>
<td>$\text{FeO} (s) + 2\text{HCl} (g) = \text{FeCl}_2 (g) + \text{H}_2\text{O} (g)$</td>
<td>900 K: -13.71, 1000 K: -3.77, 1100 K: 3.72, 1200 K: 11.02, 1300 K: 19.58</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3 (s) + 6\text{HCl} (g) = 2\text{FeCl}_3 (g) + 3\text{H}_2\text{O} (g)$</td>
<td>900 K: 118.74, 1000 K: 119.12, 1100 K: 120.06, 1200 K: 104.59, 1300 K: 123.03</td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + 4\text{HCl} (g) = \text{TiCl}_4 (g) + 2\text{H}_2\text{O} (g)$</td>
<td>900 K: 129.88, 1000 K: 137.65, 1100 K: 145.55, 1200 K: 153.55, 1300 K: 161.66</td>
</tr>
<tr>
<td>$\text{FeTiO}_3 (s) + 2\text{HCl} (g) = \text{FeCl}_2 (l,g) + \text{H}_2\text{O} (g) + \text{TiO}_2 (s)$</td>
<td>900 K: -0.97, 1000 K: 8.10, 1100 K: 14.70, 1200 K: 21.12, 1300 K: 28.79</td>
</tr>
<tr>
<td>CaCl$_2$ as chlorine source</td>
<td></td>
</tr>
<tr>
<td>$\text{FeO} (s) + \text{CaCl}_2 (s,l) = \text{FeCl}_2 (l,g) + \text{CaO} (s)$</td>
<td>900 K: 99.73, 1000 K: 98.47, 1100 K: 96.38, 1200 K: 95.57, 1300 K: 96.23</td>
</tr>
<tr>
<td>$\text{FeO} (s) + \text{TiO}_2 (s) + \text{CaCl}_2 (s,l) = \text{FeCl}_2 (l,g) + \text{CaTiO}_3 (s)$</td>
<td>900 K: 13.29, 1000 K: 11.23, 1100 K: 8.33, 1200 K: 6.67, 1300 K: 6.49</td>
</tr>
<tr>
<td>$\text{FeTiO}_3 (s) + \text{CaCl}_2 (s,l) = \text{FeCl}_2 (l,g) + \text{CaTiO}_3 (s)$</td>
<td>900 K: 26.03, 1000 K: 23.10, 1100 K: 19.31, 1200 K: 16.77, 1300 K: 15.69</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3 (s) + 3\text{CaCl}_2 (g) = 2\text{FeCl}_3 (g) + 3\text{CaO} (s)$</td>
<td>900 K: 459.06, 1000 K: 425.85, 1100 K: 398.06, 1200 K: 375.02, 1300 K: 352.97</td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + 2\text{CaCl}_2 (s,l) = \text{TiCl}_4 (g) + 2\text{CaO} (s)$</td>
<td>900 K: 356.76, 1000 K: 342.14, 1100 K: 330.88, 1200 K: 322.65, 1300 K: 314.95</td>
</tr>
<tr>
<td>CaCl$_2$ (s,l) + H$_2$O(g) = CaO(s) + 2HCl (g)</td>
<td>900 K: 113.44, 1000 K: 102.24, 1100 K: 92.67, 1200 K: 84.55, 1300 K: 76.65</td>
</tr>
<tr>
<td>$\text{FeTiO}_3 (s) + 2\text{HCl} (g) + \text{CaO} (s) = \text{FeCl}_2 (l,g) + \text{CaTiO}_3 (s) + \text{H}_2\text{O} (g)$</td>
<td>900 K: -87.41, 1000 K: -79.14, 1100 K: -73.35, 1200 K: -67.77, 1300 K: -60.95</td>
</tr>
<tr>
<td>2C(s) + O$_2$(g) = 2CO(g)</td>
<td>900 K: -382.82, 1000 K: -400.52, 1100 K: -418.11, 1200 K: -435.59, 1300 K: -452.96</td>
</tr>
</tbody>
</table>

a: References
### Reactions

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Gibbs energy change, $\Delta G_{\text{f}}^n$ or $\Delta G_{\text{r}}^n$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900 K</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + \text{FeO}(s) = \text{FeTiO}_3(s)$</td>
<td>-12.738</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + \text{CaO}(s) = \text{CaTiO}_3(s)$</td>
<td>-86.438</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + \text{Fe}_2\text{O}_3(s) = \text{Fe}_2\text{TiO}_3(s)$</td>
<td></td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + \text{MgO}(s) = \text{MgTiO}_3(s)$</td>
<td>-24.291</td>
</tr>
<tr>
<td>$\text{MgCl}_2$ as chlorine source</td>
<td></td>
</tr>
<tr>
<td>$\text{FeO}(s) + \text{MgCl}_2(s,l) = \text{FeCl}_2(l,g) + \text{MgO}(s)$</td>
<td>-22.385</td>
</tr>
<tr>
<td>$\text{FeTiO}_3(s) + \text{MgCl}_2(s,l) = \text{FeCl}_2(l,g) + \text{TiO}_2(s) + \text{MgO}(s)$</td>
<td>-9.647</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3(s) + 3\text{MgCl}_2(g) = 2\text{FeCl}_3(g) + 3\text{MgO}(s)$</td>
<td>92.71</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + 2\text{MgCl}_2(s,l) = \text{TiCl}_4(g) + 2\text{MgO}(s)$</td>
<td>112.529</td>
</tr>
<tr>
<td>$\text{MgCl}_2(s,l) + \text{H}_2\text{O}(g) = \text{MgO}(s) + 2\text{HCl}(g)$</td>
<td>8.675</td>
</tr>
<tr>
<td>$\text{FeO}(s) + 2\text{HCl}(g) = \text{FeCl}_2(g) + \text{H}_2\text{O}(g)$</td>
<td>-13.71</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + 2\text{FeO}(s) = 4\text{HCl}(g) = \text{TiCl}_4(g) + 2\text{H}_2\text{O}(g)$</td>
<td>118.735</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3(s) + 6\text{HCl}(g) = 2\text{FeCl}_3(g) + 3\text{H}_2\text{O}(g)$</td>
<td>129.879</td>
</tr>
<tr>
<td>$\text{FeTiO}_3(s) + 2\text{HCl}(g) + \text{CaO}(s) = \text{FeCl}_2(l,g) + \text{CaTiO}_3(s) + \text{H}_2\text{O}(g)$</td>
<td>-9.72</td>
</tr>
<tr>
<td>$\text{CaCl}_2$ as chlorine source</td>
<td></td>
</tr>
<tr>
<td>$\text{FeO}(s) + \text{CaCl}_2(s,l) = \text{FeCl}_2(l,g) + \text{CaO}(s)$</td>
<td>99.73</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3(s) + \text{CaCl}_2(s,l) = \text{FeCl}_2(l,g) + \text{CaTiO}_3(s)$</td>
<td>13.292</td>
</tr>
<tr>
<td>$\text{FeTiO}_3(s) + \text{CaCl}_2(s,l) = \text{FeCl}_2(l,g) + \text{CaTiO}_3(s)$</td>
<td>26.03</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3(s) + 3\text{CaCl}_2(g) = 2\text{FeCl}_3(g) + 3\text{CaO}(s)$</td>
<td>459.055</td>
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<tr>
<td>$\text{TiO}_2(s) + 2\text{CaCl}_2(s,l) = \text{TiCl}_4(g) + 2\text{CaO}(s)$</td>
<td>356.759</td>
</tr>
<tr>
<td>$\text{CaCl}_2(s,l) + \text{H}_2\text{O}(g) = \text{CaO}(s) + 2\text{HCl}(g)$</td>
<td>113.440</td>
</tr>
<tr>
<td>$\text{FeTiO}_3(s) + 2\text{HCl}(g) + \text{CaO}(s) = \text{FeCl}_2(l,g) + \text{CaTiO}_3(s) + \text{H}_2\text{O}(g)$</td>
<td>-87.410</td>
</tr>
<tr>
<td>$2\text{C}(s) + \text{O}_2(g) = 2\text{CO}(g)$</td>
<td>-382.82</td>
</tr>
<tr>
<td>$\text{TiO}_2(s) + 2\text{Ca}(s) = \text{Ti}(s) + 2\text{CaO}(s)$</td>
<td>-302.46</td>
</tr>
<tr>
<td>$\text{CaTiO}_3(s) + 2\text{Ca}(s) = \text{Ti}(s) + 3\text{CaO}(s)$</td>
<td>-216.02</td>
</tr>
</tbody>
</table>

**References**

Gibbs energy change of formation and reaction in the Fe-Ti-O system.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Gibbs energy change, $\Delta G_T$ or $\Delta G_r$, (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100 K</td>
<td>1200 K</td>
</tr>
<tr>
<td>Fe(s) + 0.5 O$_2$(g) = FeO(s)</td>
<td>-200.709</td>
<td>-194.362</td>
</tr>
<tr>
<td></td>
<td>-192.476</td>
<td>-185.817</td>
</tr>
<tr>
<td></td>
<td>-200.670</td>
<td>-271.184</td>
</tr>
<tr>
<td></td>
<td>-190.021</td>
<td>-183.792</td>
</tr>
<tr>
<td>Ti(s) + O$_2$(g) = TiO$_2$(s)</td>
<td>-744.912</td>
<td>-727.229</td>
</tr>
<tr>
<td></td>
<td>-745.367</td>
<td>-727.312</td>
</tr>
<tr>
<td></td>
<td>-744.807</td>
<td>-727.113</td>
</tr>
<tr>
<td></td>
<td>-742.567</td>
<td>-724.883</td>
</tr>
<tr>
<td></td>
<td>-717.417</td>
<td>-700.250</td>
</tr>
<tr>
<td>Fe(s) + Ti(s) + 1.5 O$_2$(g) = FeTiO$_3$(s)</td>
<td>-956.608</td>
<td>-931.690</td>
</tr>
<tr>
<td>2 Fe(s) + Ti(s) + 2 O$_2$(g) = Fe$_2$TiO$_4$(s)</td>
<td>-1164.697</td>
<td>-1133.483</td>
</tr>
<tr>
<td></td>
<td>-1164.870</td>
<td>-1133.57</td>
</tr>
<tr>
<td>TiO$_2$(s) + Fe(s) + 0.5 O$_2$(g) = FeTiO$_3$(s)</td>
<td>-211.696</td>
<td>-204.461</td>
</tr>
<tr>
<td></td>
<td>-202.3</td>
<td>-199.171</td>
</tr>
<tr>
<td></td>
<td>-209.946</td>
<td>-204.558</td>
</tr>
<tr>
<td>TiO$_2$(s) + 2 Fe(s) + O$_2$(g) = Fe$_2$TiO$_4$(s)</td>
<td>-417.785</td>
<td>-406.254</td>
</tr>
<tr>
<td></td>
<td>-419.503</td>
<td>-406.258</td>
</tr>
<tr>
<td>TiO$_2$(s) + FeO(s) = FeTiO$_3$(s)</td>
<td>-10.987</td>
<td>-10.099</td>
</tr>
<tr>
<td></td>
<td>-20.042</td>
<td>-18.833</td>
</tr>
<tr>
<td></td>
<td>-12.6</td>
<td>1, 5</td>
</tr>
<tr>
<td></td>
<td>-12.6</td>
<td>4, 5</td>
</tr>
<tr>
<td></td>
<td>-21.381</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>-23.1</td>
<td>5, 8</td>
</tr>
<tr>
<td>TiO$_2$(s) + 2 FeO(s) = Fe$_2$TiO$_4$(s)</td>
<td>-18.367</td>
<td>-17.53</td>
</tr>
<tr>
<td></td>
<td>-34.551</td>
<td>-34.707</td>
</tr>
<tr>
<td></td>
<td>-13.8</td>
<td>1, 5</td>
</tr>
<tr>
<td></td>
<td>-13.9</td>
<td>4, 5</td>
</tr>
</tbody>
</table>

$\Delta G_r = -30 \sim -9 \text{ kJ/mol}$

$\text{TiO}_x + n \text{ FeO} = \text{TiFe}_n\text{O}_{1+x+n}$

Ti ore is considered as the mixture of TiO$_x$ + FeO because $\Delta G_r$ of TiFe$_x$O$_y$ is not large as compared to those of the redox reactions in the related system.

References

a: Interpolated
Mechanism of iron removal (FeO<sub>x</sub> chlorination)

Fe-Cl-O system, \( T = 1300 \text{ K} \)

Chemical potential diagram of the Fe-Cl-O system at 1300 K.

I:
\[
\begin{align*}
    \text{H}_2\text{O} (g) + \text{CaCl}_2 (l) & \rightarrow \text{HCl} (g) + \text{CaO} (s) \\
    \text{FeO}_x (\text{FeTiO}_x, s) + \text{HCl} (g) & \rightarrow \text{FeCl}_2 (l, g) + \text{H}_2\text{O} (g)
\end{align*}
\]

II:
\[
\begin{align*}
    \text{FeO}_x (\text{FeTiO}_x, s) + \text{CaCl}_2 (l) & \rightarrow \text{FeCl}_x (g) + \text{CaO} (\text{CaTiO}_x s) \\
    a_{\text{CaO}} & << 1
\end{align*}
\]

FeO<sub>x</sub> can be chlorinated using CaCl<sub>2</sub> + H<sub>2</sub>O.
Mechanism of iron removal (TiO$_x$ chlorination)

TiO$_x$ can not be chlorinated using CaCl$_2$, or CaCl$_2$+H$_2$O.

Chemical potential diagram of the Ti-Cl-O system at 1300 K.
Mechanism of iron removal (Ti ore chlorination)

Fe-Cl-O and Ti-Cl-O systems, $T = 1300$ K

Combined chemical potential diagram of the Fe-Cl-O (dotted line) and Ti-Cl-O (solid line) systems at 1300 K.

**FeO$_x$ (FeTiO$_x$, $s$) + HCl ($g$)**

$\rightarrow$ **FeCl$_x$ ($g$)↑ + H$_2$O ($g$)**

**FeO$_x$ (FeTiO$_x$, $s$) + CaCl$_2$ ($l$)**

$\rightarrow$ **FeCl$_x$ ($g$)↑ + CaO (CaTiO$_x$, $s$)**

$\underline{a_{\text{CaO}}<<1}$

FeO$_x$ can be chlorinated using CaCl$_2$+H$_2$O.

TiO$_x$ can not be chlorinated using CaCl$_2$, or CaCl$_2$+H$_2$O.
Reciprocal temperature, $1000 \frac{1}{T} / K^{-1}$

Vapor pressure, $\log p_i$ (atm)

- $TiCl_2 (s)$
- $TiCl_3 (s)$
- $TiCl_4 (l)$
- $FeCl_2 (s,l)$
- $FeCl_3 (s,l)$
- $Si (s,l)$
- $Al (s,l)$
- $AlCl_3 (s,l)$
- $Ti (s,l)$
- $Fe (s,l)$
Fig. Vapor pressure of aluminium and silicon chlorides as a function of reciprocal temperature.
Ellingham diagram of some selected oxides

Only Ca can be utilized as reductant for the production of metallic Ti with low oxygen content directly from Ti ore.

\[ \text{TiO}_2 (s) + \text{Ca} (g) \rightarrow \text{Ti} (s) + \text{CaO} (s) \]

~500ppmO

Only Ca can be utilized as reductant for the production of metallic Ti with low oxygen content directly from Ti ore.

\[ \text{TiO}_2 (s) + \text{Ca} (g) \rightarrow \text{Ti} (s) + \text{CaO} (s) \]

~500ppmO
Vapor pressure of some selected metals and chlorides

Vapor pressure of selected metals and chlorides.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chloride</th>
<th>Vapor Pressure, $\log p_i$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>NaCl</td>
<td>-12</td>
</tr>
<tr>
<td>K</td>
<td>KCl</td>
<td>-10</td>
</tr>
<tr>
<td>Mg</td>
<td>MgCl$_2$</td>
<td>-8</td>
</tr>
<tr>
<td>Ca</td>
<td>CaCl$_2$</td>
<td>-6</td>
</tr>
<tr>
<td>Ti</td>
<td>TiCl$_2$</td>
<td>-4</td>
</tr>
<tr>
<td>TiCl$_3$</td>
<td></td>
<td>-2</td>
</tr>
</tbody>
</table>

1273 K (Reaction temperature)

Range of vapor pressure feasible for supplying reductants in vapor form

The vapor pressure of Ca: 0.024 atm @ 1273 K

Ca reductant can be supplied as vapor form for reducing Ti ore in the PRP.
Impurity removal

\[
\text{SiO}_2 \text{ (in ore)} + 2 \text{MgCl}_2 \text{ (Flux)} \rightarrow \text{SiCl}_4 \text{ (g)} + 2 \text{MgO \ (s)}
\]

Si-Cl-O system, \( T = 1300 \text{ K} \)

- \( \text{SiO}_2 \) (s)
- \( \text{Si} \) (s)
- \( \text{SiCl}_4 \) (g)
- \( \text{CaO \ (s)} / \text{CaCl}_2 \text{ (l) eq.} \)
- \( \text{CO \ (g)} / \text{CO}_2 \text{ (g) eq.} \)
- \( \text{H}_2 \text{ (g)} / \text{H}_2\text{O (g) eq.} \)
- \( \text{C \ (s)} / \text{CO \ (g) eq.} \)
- \( \text{H}_2\text{O (g)} / \text{HCl \ (g) eq.} \)
- \( \text{MgO \ (s)} / \text{MgCl}_2 \text{ (g) eq.} \)
Ti-Ca binary phase diagram

Weight Percent Calcium

Temperature °C

(βTi) + L

(αTi) + L

(αTi) + (βCa)

882°C

842°C (MP)

0 10 20 30 40 50 60 70 80 90 100

Ti

0 10 20 30 40 50 60 70 80 90 100

Atomic Percent Calcium

Ca
Selective chlorination experiment

Experimental apparatus for the selective chlorination of titanium ore using radio frequency (RF) furnace.

Deposit obtained after exp.}
Dimensions and appearance of stainless steel susceptor for the RF furnace used for the selective chlorination of titanium ore.
Illustrations and appearance of the sample in the graphite crucible installed in the RF furnace:
## Experiment conditions

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Mass of feed materials, w / g</th>
<th>Mixture or layer sample (from bottom to top)</th>
<th>Reaction temp., T / K</th>
<th>Reaction time, t / h</th>
<th>Atmosphere</th>
<th>Flow ratio, cc / min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCD</td>
<td>3.01</td>
<td>Mixture</td>
<td>1173</td>
<td>6</td>
<td>N₂ + H₂O</td>
<td>full flow</td>
</tr>
<tr>
<td>SCO</td>
<td>4.00</td>
<td>Mixture</td>
<td>1173</td>
<td>3</td>
<td>N₂ + H₂O</td>
<td>50</td>
</tr>
<tr>
<td>SCP</td>
<td>3.00</td>
<td>Mixture</td>
<td>1173</td>
<td>3</td>
<td>N₂ + H₂O</td>
<td>50</td>
</tr>
<tr>
<td>SCR</td>
<td>3.00</td>
<td>Mixture</td>
<td>1273</td>
<td>6</td>
<td>N₂ + H₂O</td>
<td>50</td>
</tr>
<tr>
<td>SCS</td>
<td>3.00</td>
<td>Mixture</td>
<td>1293</td>
<td>6</td>
<td>N₂ + H₂O</td>
<td>50</td>
</tr>
</tbody>
</table>

a: Natural ilmenite ore produced in Vietnam after pulverization.
Chapter 3

Results of selective chlorination (1): Observation

(a) Photo taken during the experiment: white smoke
(b) The obtained sample in the graphite crucible: sintered sample
(c) Deposit inside the quartz tube: white deposit
## Results of selective chlorination (2): XRF

Analytical results of the obtained sample after selective chlorination.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Concentration of element i, $C_i$ (mass%)(^a)</th>
<th>$C_{Fe} / C_{Ti}$</th>
<th>Iron removal ratio, $R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Si</td>
<td>Ti</td>
</tr>
<tr>
<td>Ti ore(^b)</td>
<td>0.07</td>
<td>0.44</td>
<td>43.83</td>
</tr>
<tr>
<td>SCD</td>
<td>n.d.</td>
<td>1.27</td>
<td>80.10</td>
</tr>
<tr>
<td>SCO</td>
<td>n.d.</td>
<td>3.17</td>
<td>64.91</td>
</tr>
<tr>
<td>SCP</td>
<td>n.d.</td>
<td>14.15</td>
<td>54.22</td>
</tr>
<tr>
<td>SCS</td>
<td>n.d.</td>
<td>14.71</td>
<td>78.98</td>
</tr>
</tbody>
</table>

\(^a\): Determined by X-ray fluorescence analysis (XRF), the value excludes carbon and gaseous elements, n.d. = not detected (below 0.01 %) 
\(^b\): Natural ilmenite ore produced in Vietnam. 
\(c\): $R = 100 \times \{1 - (C_{Fe, after} / C_{Ti, after}) / (C_{Fe, before} / C_{Ti, before})\}$. 

**After experiment: $C_{Fe}^{†}: 51.3\% \rightarrow 3.2\%$**

Fe was removed from Ti ore successfully.
Results of selective chlorination (3): XRD

XRD patterns of (a) the residue in crucible and (b) the deposit inside the quartz tube. (Exp. SCS)

The generation of CaTiO$_3$ was considered to be beneficial for removing iron from Ti ore.

The generation of FeCl$_2$ indicates that iron was removed from Ti ore as the form of FeCl$_2$. 
Discussion: Mechanism of selective chlorination

Generation of CaTiO$_3$ and FeCl$_2$

The reactions were considered as follows:

I: \[ \text{H}_2\text{O} \ (g) + \text{CaCl}_2 \ (l) \rightarrow 2 \text{HCl} \ (g) + \frac{\text{CaO} \ (\text{CaTiO}_x, \ s)}{a_{\text{CaO}} \ll 1} \]

\[ \text{FeO}_x \ (\text{FeTiO}_x, \ s) + \text{HCl} \ (g) \rightarrow \text{FeCl}_2 \ (l, \ g) + \text{H}_2\text{O} \ (g) \]

or

II: \[ \text{FeO}_x \ (\text{FeTiO}_x, \ s) + \text{CaCl}_2 \ (l) \rightarrow \text{FeCl}_2 \ (l, \ g) + \frac{\text{CaO} \ (\text{CaTiO}_x, \ s)}{a_{\text{CaO}} \ll 1} \]
Summary on iron removal from low-grade Ti ore by selective chlorination

1. Iron removal from Ti ore was carried out successfully.

   In a certain experimental condition: $C_{Fe}: 51.3\% \rightarrow 3.2\%$

2. The mechanism of the selective chlorination reactions was considered as follows:

   $\text{FeO}_x (\text{FeTiO}_x, s) + \text{HCl} (g) \rightarrow \text{FeCl}_2 (l, g) + \text{H}_2\text{O} (g)$

   or

   $\text{FeO}_x (\text{FeTiO}_x, s) + \text{CaCl}_2 (l) \rightarrow \text{FeCl}_2 (l, g) + \text{CaO (CaTiO}_x, s)$
## Table Analytical results of titanium ores used in this study. 051230

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Concentration of element $i$, $C_i$ (mass%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>XRF file name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Si</td>
</tr>
<tr>
<td>ilmenaite&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.60</td>
<td>2.30</td>
</tr>
<tr>
<td>ilmenaite&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.75</td>
<td>2.19</td>
</tr>
<tr>
<td>UGI&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.05</td>
<td>0.42</td>
</tr>
<tr>
<td>UGI&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.04</td>
<td>0.36</td>
</tr>
</tbody>
</table>

<sup>a</sup> Value determined by XRF analysis, n.d. notes not detected (below 0.01 mass%).

<sup>b</sup> Natural ilmenite ore produced in Australia.

<sup>c</sup> Natural ilmenite ore produced in Viet Nam.

<sup>d</sup> Up-graded ilmenite by the Beacher process (see Fig. 1-7). The ore was produced in Australia.

<sup>e</sup> Up-graded ilmenite by the Benilite process (see Fig. 1-6). The ore was produced in India.
<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Mass of feed materials, w / g</th>
<th>Susceptor Version</th>
<th>Foil</th>
<th>Mixture or layer sample (from bottom to top)</th>
<th>Reaction temp., T / K</th>
<th>Reaction time, t' / hr</th>
<th>Atmosphere</th>
<th>Flow ratio, cc / min.</th>
<th>Note&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCA</td>
<td>3.03 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1073</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O full flow</td>
<td>041129</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCB</td>
<td>3.00 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1073</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O full flow</td>
<td>041210</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCC</td>
<td>3.04 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni layer (CaCl&lt;sub&gt;2&lt;/sub&gt;, C, ore)</td>
<td>1073</td>
<td>6 Ar + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>050127</td>
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</tr>
<tr>
<td>SCD</td>
<td>3.01 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1173</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O full flow</td>
<td>050404</td>
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<tr>
<td>SCE</td>
<td>3.01 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1048</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
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<td>2 Ni Mixture</td>
<td>1051</td>
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<td>2 Ni Mixture</td>
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<td>2 Ni Mixture</td>
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<td>2 Ni Mixture</td>
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<td>2 Ni Mixture</td>
<td>1023</td>
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<td>3.00 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1023</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
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<td>SCL</td>
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<td>2 Ni Mixture</td>
<td>1073</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
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<td>2 Ni Mixture</td>
<td>1173</td>
<td>3 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>060508</td>
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<td>SCN</td>
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<td>2 Ni Mixture</td>
<td>1173</td>
<td>3 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>060509</td>
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<td>SCO</td>
<td>3.00 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1173</td>
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<td>2 Ni Mixture</td>
<td>1173</td>
<td>3 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
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<td>2 Ni Mixture</td>
<td>1253</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>060517</td>
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<td>SCR</td>
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<td>2 Ni Mixture</td>
<td>1273</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>060519</td>
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<td></td>
<td></td>
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<td>3.00 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1293</td>
<td>6 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>060524</td>
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<td>3.00 CaCl&lt;sub&gt;2&lt;/sub&gt; C H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Ni Mixture</td>
<td>1293</td>
<td>12 N&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O 50</td>
<td>060529</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: Natural ilmenite ore produced in Vietnam after pulverization.

b: Up-graded ilmenite by the Benilite process was produced in India.

c: Experiment date.
### Table

Analytical results of the sample after heating (position: bottom).

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Concentration of element $i$, $C_i$ (mass%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fe / Ti ratio, $C_{Fe} / C_{Ti}$</th>
<th>Iron removal ratio, $R^d$ (%)</th>
<th>Note&lt;sup&gt;c&lt;/sup&gt;</th>
<th>XRF file name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al  Si  Ti  V  Cr  Mn  Fe  Ni  Nb</td>
<td>Before Exp.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>After Exp.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCA</td>
<td>0.02 3.90 74.52 1.59 n.d. 3.58 15.16 0.26 0.98</td>
<td>1.09</td>
<td>0.20</td>
<td>81</td>
<td>04112904112901</td>
</tr>
<tr>
<td>SCB</td>
<td>0.09 12.69 68.28 1.07 n.d. 3.60 13.29 0.18 0.79</td>
<td>1.09</td>
<td>0.19</td>
<td>82</td>
<td>04121004121004</td>
</tr>
<tr>
<td>SCC</td>
<td>n.d. 0.35 70.54 1.14 n.d. 3.06 24.37 0.19 0.35</td>
<td>1.09</td>
<td>0.35</td>
<td>68</td>
<td>05012705012702</td>
</tr>
<tr>
<td>SCD</td>
<td>n.d. 1.27 80.10 1.11 n.d. 2.42 13.98 0.03 1.10</td>
<td>1.09</td>
<td>0.17</td>
<td>84</td>
<td>05040405040401</td>
</tr>
<tr>
<td>SCE</td>
<td>n.d. 0.61 12.26 0.25 n.d. 2.58 80.36 3.82 0.12</td>
<td>1.09</td>
<td>6.56</td>
<td>-502</td>
<td>05060805060801</td>
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<tr>
<td>SCF</td>
<td>n.d. 0.71 37.72 0.70 n.d. 4.02 54.40 2.23 0.23</td>
<td>1.09</td>
<td>1.44</td>
<td>-32</td>
<td>05060905060901</td>
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<tr>
<td>SCG</td>
<td>0.05 2.15 90.03 2.22 n.d. 0.28 3.77 0.17 1.34</td>
<td>0.01</td>
<td>0.04</td>
<td>-318</td>
<td>05061405061401</td>
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<tr>
<td>SCH</td>
<td>n.d. 6.96 32.73 0.41 n.d. 3.26 53.50 2.76 0.38</td>
<td>1.09</td>
<td>1.63</td>
<td>-50</td>
<td>06041006041001</td>
</tr>
<tr>
<td>SCI</td>
<td>n.d. 0.48 43.24 0.52 n.d. 1.23 47.83 6.37 0.32</td>
<td>1.09</td>
<td>1.11</td>
<td>-1</td>
<td>06041306041301</td>
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<tr>
<td>SCJ</td>
<td>n.d. 1.00 39.67 0.67 n.d. 5.05 48.69 4.08 0.84</td>
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<td>1.23</td>
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<td>SCK</td>
<td>n.d. 2.63 24.59 0.51 n.d. 3.13 48.43 20.33 0.39</td>
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<td>1.97</td>
<td>-81</td>
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<tr>
<td>SCL</td>
<td>n.d. 4.32 34.41 1.09 n.d. 5.27 48.90 5.12 0.88</td>
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<td>1.42</td>
<td>-30</td>
<td>06042606042601</td>
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<tr>
<td>SCM</td>
<td>n.d. 12.51 31.46 1.36 n.d. 11.07 37.41 4.94 1.24</td>
<td>1.09</td>
<td>1.19</td>
<td>-9</td>
<td>06050806050801</td>
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<tr>
<td>SCN</td>
<td>n.d. 8.42 34.09 3.33 n.d. 11.87 38.45 2.84 0.99</td>
<td>1.09</td>
<td>1.13</td>
<td>-3</td>
<td>06050906050901</td>
</tr>
<tr>
<td>SCO</td>
<td>n.d. 3.17 64.91 1.23 n.d. 4.88 24.33 0.32 1.15</td>
<td>1.09</td>
<td>0.37</td>
<td>66</td>
<td>06051006051001</td>
</tr>
<tr>
<td>SCP</td>
<td>n.d. 14.15 54.22 2.23 0.17 5.08 22.22 0.66 1.27</td>
<td>1.09</td>
<td>0.41</td>
<td>62</td>
<td>06051106051101</td>
</tr>
<tr>
<td>SCQ</td>
<td>n.d. 22.73 66.03 0.99 0.10 1.13 8.31 0.02 0.70</td>
<td>1.09</td>
<td>0.13</td>
<td>88</td>
<td>06051706051701</td>
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<tr>
<td>SCR</td>
<td>n.d. 24.25 52.69 0.86 n.d. 3.86 16.50 0.43 1.42</td>
<td>1.09</td>
<td>0.31</td>
<td>71</td>
<td>06051906051901</td>
</tr>
<tr>
<td>SCS</td>
<td>n.d. 14.71 78.98 0.80 0.18 0.92 3.17 0.59 0.65</td>
<td>1.09</td>
<td>0.04</td>
<td>96</td>
<td>06052406052401</td>
</tr>
<tr>
<td>SCT</td>
<td>n.d. 8.37 87.93 0.74 0.41 0.46 1.54 0.29 0.27</td>
<td>1.09</td>
<td>0.02</td>
<td>98</td>
<td>06052406052401</td>
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</table>

<sup>a</sup>: Value determined by XRF analysis, the value excludes carbon and gaseour elements, and n.d. notes not detected (below 0.01 mass%).

<sup>b</sup>: This data isthe same data shown in Table 3-7, because this sample is powder.

<sup>c</sup>: See Table 3-2 for reference.

<sup>d</sup>: $R = 100 \times \{1 - (C_{Fe, after} / C_{Ti, after}) / (C_{Fe, before} / C_{Ti, before})\}$, This iron removal ratio includes large uncertainties, and listed for reference.

<sup>e</sup>: Experimental date.
<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Mass of feed materials, w / g</th>
<th>Susceptor Version</th>
<th>Foil</th>
<th>Mixture or layer sample (from bottom to top)</th>
<th>Reaction temp., T / K</th>
<th>Reaction time, t' / hr</th>
<th>Atmosphere</th>
<th>Flow ratio, cc / min.</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMA</td>
<td>2.04</td>
<td>1.44</td>
<td>2</td>
<td>Ni</td>
<td>1100</td>
<td>6</td>
<td>N₂ + H₂O</td>
<td>50</td>
<td>050805</td>
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<td>SMB</td>
<td>2.05</td>
<td>1.40</td>
<td>2</td>
<td>Ni</td>
<td>1300</td>
<td>Failure</td>
<td>N₂ + H₂O</td>
<td>-</td>
<td>050816</td>
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<tr>
<td>SMC</td>
<td>2.00</td>
<td>1.14</td>
<td>2</td>
<td>Ni</td>
<td>1000</td>
<td>6</td>
<td>N₂ + H₂O</td>
<td>50</td>
<td>050818</td>
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</tbody>
</table>

a: Natural ilmenite ore produced in Vietnam after pulverization.
b: Up-graded ilmenite by the Benilite process was produced in India.
c: Experiment date.
Institute of Industrial Science, The University of Tokyo

2007 Annual Meeting, February 25-March 1, 2007, Orlando, FL, USA

060704 XRD

- FeCl₂(H₂O)₄ (JCPDS #71-0668)

Blank
Scanning electron microscopic image of titanium powder obtained after calciothermic reduction of iron removed titanium ore (Exp. E-red.).
<table>
<thead>
<tr>
<th>Materials</th>
<th>Form</th>
<th>Purity (%)</th>
<th>Note / Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Powder</td>
<td>98.0 up</td>
<td>Toho Titanium Co., Ltd.</td>
</tr>
<tr>
<td>Ti sponge</td>
<td>Granule</td>
<td>99.2*</td>
<td>Toho Titanium Co., Ltd.</td>
</tr>
<tr>
<td>FeCl$_2$</td>
<td>Powder</td>
<td>99.0</td>
<td>Kojyundo Chemical Laboratory Co., Ltd.</td>
</tr>
</tbody>
</table>

*: Determined by X-ray fluorescence analysis (XRF).
### Table: Experimental conditions of chlorine recovery

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Mass of feed materials, $w_i$ / g</th>
<th>Mass Ratio $w_{Ti} / w_{FeCl_2}$</th>
<th>Reaction temp., $T$ / K</th>
<th>Reaction time, $t'$ / h</th>
<th>Atmosphere</th>
<th>Pressure $p$ / atm</th>
<th>Note $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA$^a$</td>
<td>0.33 1.90 5.27</td>
<td>5.79 1100 1</td>
<td>Ar</td>
<td>-0.08 -0.06</td>
<td></td>
<td>041222</td>
<td></td>
</tr>
<tr>
<td>CB$^a$</td>
<td>0.30 1.75 3.18</td>
<td>5.79 1100 1</td>
<td>Ar</td>
<td>-0.08 -0.06</td>
<td></td>
<td>050104</td>
<td></td>
</tr>
<tr>
<td>CC$^a$</td>
<td>0.32 1.72 -</td>
<td>5.36 1100 1</td>
<td>Ar</td>
<td>-0.08 -0.06</td>
<td></td>
<td>050121</td>
<td></td>
</tr>
<tr>
<td>CD$^b$</td>
<td>0.49 2.76 3.25</td>
<td>5.63 1100 3</td>
<td>Ar</td>
<td>-0.08 -0.05</td>
<td></td>
<td>060621</td>
<td></td>
</tr>
<tr>
<td>CE$^b$</td>
<td>0.51 2.86 5.47</td>
<td>5.61 1100 3</td>
<td>Ar</td>
<td>-0.08 -0.06</td>
<td></td>
<td>060915</td>
<td></td>
</tr>
</tbody>
</table>

a: Experiment date.
b: Ti powder was used in this experiment.
c: Ti granules was used in this experiment.
d: Ti turing was used in this experiment.
Experiment apparatus (3)

- Glass wool
- Quartz tube
- Graphite crucible
- Vacuum pump
- Ar gas
- Silicone rubber plug
- NaOH gas trap
- Sample mixture: e.g., FeCl₂ + Ti powder

( Deposits after the experiment)

Exp. # CE, CF
Observation

Assembled quartz tube after experiment.

The form of the obtained residue and deposit after experiment.

Silicone plug after experiment
Deposit on the surface of the NaOH gas trap
Deposit inside the quartz tube
Residue in the graphite crucible

Raw materials:
- Ti powder
- FeCl₂ powder
- Ti granule
- FeCl₂ powder
- Ti turning
- FeCl₂ powder

Melting point of FeCl₂: 950 K @ 1 atm
Melting point of TiCl₂: 408 K @ 1 atm

Deposit on the surface of the NaOH gas trap
Flake (Brown)
Residue (Black)

Institute of Industrial Science, The University of Tokyo
2007 Annual Meeting, February 25-March 1, 2007, Orlando, FL, USA
Ti granule: XRD

Int. (a.u.)

10 20 30 40 50 60 70 80 90 100

Angle, $2\theta$ (deg.)

○: $\alpha$-Ti (JCPDS #44-1294)
●: $\alpha$-Fe (JCPDS #06-0696)

Fe phase appeared in the obtained residue.

Ti (s) + FeCl$_2$ (l, g) $\rightarrow$ TiCl$_4$ (g) + Fe (s)
Analytical results of the samples before and after heating, and the deposits obtained within the quartz tube and on the surface of the NaOH gas trap after heating.

<table>
<thead>
<tr>
<th>Exp. CF</th>
<th>Concentration of element $i$, $C_i$ (mass%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Initial sample in the graphite crucible</td>
<td>13.6$^a$</td>
</tr>
<tr>
<td>before heating</td>
<td></td>
</tr>
<tr>
<td>Residue in the graphite crucible</td>
<td>29.1$^b$</td>
</tr>
<tr>
<td>Deposit inside the quartz tube</td>
<td>0.06$^b$</td>
</tr>
<tr>
<td>Deposit on the surface of the NaOH gas trap</td>
<td>0.04$^b$</td>
</tr>
</tbody>
</table>

$^a$: Calculated.
$^b$: Determined by X-ray fluorescence analysis (XRF).

Black coat was obtained on the surface of the residue.
The residue is of magnetic character.
Fe element exists in the residue after heating.
Discussion (3)

Although Ti in Ti granule or turning was extracted by FeCl₂, the efficiency of the recovery of Ti scraps is low and the reaction speed in the system decreased when Ti granule or turning was used as the feed material.

The reaction speed was affected by the morphology of the Ti scraps.
The purpose of this study

Development of a new process for producing high-purity Ti powder

- High-productivity, low-cost process has to be developed for producing high-purity Ti.

Preform reduction process (PRP)

- Feed preform (TiO₂ feed + flux)
- Reductant vapor
- Reductant (R = Ca, or Ca-X alloy)
Preform Reduction Process (PRP) ?

\[
\text{TiO}_2 (s, \text{in feed preform}) + \text{Ca} (g) \rightarrow \text{Ti} (s, \text{powder}) + \text{CaO} (s, \text{flux})
\]
Features of PRP

Advantages of PRP: “simple and low-cost process”
- Suitable for uniform reduction
- Flexible scalability
- Possible to control the morphology of powder by varying the flux content in the preform
- Possible to prevent the contamination from reaction container
- Amount of waste solution is minimized
- Molten salt as a flux can be reduced compared to other direct reduction process

Disadvantages of PRP:
- Leaching process is required
- Calcium production and handling of calcium vapor is difficult
PRP in this study

Previous study: Artificial feed materials

- TiO₂ powder
- Upgraded ilmenite (India)

Or

De-ionized ilmenite ore

Titanium Powder

99% up metallic titanium powder was obtained by using titanium oxide (TiO₂) or upgraded ilmenite (UGI) as the starting materials.

This study: Natural titanium ore (Rutile, South Africa) used as feed material

- Rutile ore (South Africa)

<table>
<thead>
<tr>
<th>XRF analysis (mass %)</th>
<th>Ti</th>
<th>Fe</th>
<th>Si</th>
<th>V</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>93.1</td>
<td>2.27</td>
<td>1.58</td>
<td>1.42</td>
<td>0.66</td>
</tr>
</tbody>
</table>

So far, it was difficult to produce high-purity Ti directly from natural Ti ore!
Titanium ore used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti</th>
<th>Si</th>
<th>Nb</th>
<th>Al</th>
<th>Fe</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Ni</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>UGI&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95.47</td>
<td>0.45</td>
<td>0.54</td>
<td>0.13</td>
<td>1.87</td>
<td>1.46</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.03</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.07</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>040524</td>
</tr>
<tr>
<td></td>
<td>95.85</td>
<td>0.37</td>
<td>0.62</td>
<td>0.04</td>
<td>2.04</td>
<td>1.04</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.05</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>040721</td>
</tr>
<tr>
<td>Rutile&lt;sup&gt;c&lt;/sup&gt;</td>
<td>93.10</td>
<td>1.58</td>
<td>0.62</td>
<td>0.66</td>
<td>2.27</td>
<td>1.42</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.16</td>
<td>0.01</td>
<td>0.16</td>
<td>0.03</td>
<td>040524</td>
</tr>
<tr>
<td></td>
<td>93.55</td>
<td>1.05</td>
<td>0.64</td>
<td>0.35</td>
<td>1.32</td>
<td>1.72</td>
<td>1.29</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.09</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ND&lt;sup&gt;d&lt;/sup&gt;</td>
<td>040721</td>
</tr>
</tbody>
</table>

a: Determined by X-ray fluorescence analysis (XRF).
b: Up-graded ilmenite produced in India by the Beacher process.
c: Natural rutile ore produced in South Africa.
d: Not detected. Below detection limit of XRF (<0.01%).
<table>
<thead>
<tr>
<th>Materials</th>
<th>Form</th>
<th>Purity or conc. (%)</th>
<th>Note / Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile(^a)</td>
<td>Powder</td>
<td>93.1(^c)</td>
<td>Produced in South Africa.</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>Powder</td>
<td>95.0 up</td>
<td>Kanto Chemicals., Inc.</td>
</tr>
<tr>
<td>Collodion(^b)</td>
<td>Aqueous</td>
<td>5.0(^d)</td>
<td>Wako Pure Chemical Industries, Ltd.</td>
</tr>
<tr>
<td>Ca</td>
<td>Chip</td>
<td>98.0 up</td>
<td>Mintech Japan K. K.</td>
</tr>
<tr>
<td>Ti</td>
<td>Sponge</td>
<td>98.0 up</td>
<td>Toho Titanium Co., Ltd.</td>
</tr>
<tr>
<td>CH(_3)COOH</td>
<td>Aqueous</td>
<td>99.7 up</td>
<td>Kanto Chemicals., Inc.</td>
</tr>
<tr>
<td>HCl</td>
<td>Aqueous</td>
<td>35.0(^d)</td>
<td>Kanto Chemicals., Inc.</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>Liquid</td>
<td>99.5 up</td>
<td>Wako Pure Chemical Industries, Ltd.</td>
</tr>
<tr>
<td>Acetone</td>
<td>Liquid</td>
<td>99.0 up</td>
<td>Wako Pure Chemical Industries, Ltd.</td>
</tr>
</tbody>
</table>

\(^a\) Natural rutile ore produced in South Africa.
\(^b\) 5 mass% nitro cellulose, 23.75 mass% ethanol, 71.25 mass% diethylether.
\(^c\) Purity of TiO\(_2\) in the ore.
\(^d\) Concentration of the solution.
### Experimental Condition of Preform Reduction Process

<table>
<thead>
<tr>
<th>Exp. # PCD</th>
<th>Mass of Sample, $w_i$/g</th>
<th>Cationic Molar, $R_{\text{Cat.}}/Ti$</th>
<th>Calcination</th>
<th>Mass of Reductant, $w_i$/g</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Flux</td>
<td>C Powder</td>
<td>Binder</td>
<td>Calcination temp., $T_{\text{cal.}}$/K</td>
</tr>
<tr>
<td>051212_1</td>
<td>6.26</td>
<td>1.74</td>
<td>0.20</td>
<td>4.93</td>
<td>0.2</td>
</tr>
<tr>
<td>_2</td>
<td>6.26</td>
<td>1.74</td>
<td>0.20</td>
<td>4.26</td>
<td>0.2</td>
</tr>
<tr>
<td>_3</td>
<td>5.65</td>
<td>2.35</td>
<td>0.20</td>
<td>5.54</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>5.65</td>
<td>2.35</td>
<td>0.20</td>
<td>5.79</td>
<td>0.3</td>
</tr>
</tbody>
</table>

a : Natural rutile ore produced in South Africa after pulverization.
b : Cationic molar ratio, $R_{\text{Cat.}}/Ti = N_{\text{Cat.}}/N_{\text{Ti}}$, where $N_{\text{Cat.}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that of titanium, respectively.
Table Experimental condition of preform reduction process.

<table>
<thead>
<tr>
<th>Exp. # PE</th>
<th>Mass of sample, $w_i$ /g</th>
<th>Cationic molar., $R_{\text{Cat.}}/\text{Ti}^c$</th>
<th>Calcination</th>
<th>Mass of Reductant, $w_i$ /g</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Flux</td>
<td>Binder</td>
<td>Calcination temp., $T_{\text{cal.}}$ / K</td>
<td>Calcination time, $t'_{\text{cal.}}$ / hr</td>
</tr>
<tr>
<td>050622_1</td>
<td>Rutile$^a$</td>
<td>Ilmenite$^b$</td>
<td>CaCl$_2$</td>
<td>Collodion</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.55</td>
<td>2.45</td>
<td>5.34</td>
<td>0.2</td>
<td>1273</td>
</tr>
<tr>
<td>2</td>
<td>7.55</td>
<td>2.45</td>
<td>8.39</td>
<td>0.2</td>
<td>1273</td>
</tr>
<tr>
<td>3</td>
<td>5.36</td>
<td>4.64</td>
<td>9.05</td>
<td>0.4</td>
<td>1273</td>
</tr>
<tr>
<td>4</td>
<td>5.36</td>
<td>4.64</td>
<td>10.18</td>
<td>0.4</td>
<td>1273</td>
</tr>
<tr>
<td>5</td>
<td>6.00</td>
<td>4.00</td>
<td>5.52</td>
<td>1.1</td>
<td>1273</td>
</tr>
<tr>
<td>6</td>
<td>6.00</td>
<td>4.00</td>
<td>5.69</td>
<td>1.1</td>
<td>1273</td>
</tr>
</tbody>
</table>

a: Natural rutile ore produced in South Africa.
b: Natural ilmenite ore produced in Vietnam after pulverization.
c: Cationic molar ratio, $R_{\text{Cat.}}/\text{Ti} = N_{\text{Cat.}}/(N_{\text{Ca}} + N_{\text{Ti}})$, where $N_{\text{Cat.}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that.
Ti ore → Flux → Binder → Mixing → Slurry

Rutile + CaCl$_2$ + Binder

- $T$: Room temp., $t'$: 6 h
- e.g. 40mm × 20mm × 8mm

Preform fabrication

Feed preform

Calcination/iron removal → FeCl$_x$

Sintered feed preform

Calcium vapor

Reduction

- $T$: 1273 K, $t'$: 6 ~10 h

Reduced preform

Leaching → Waste solution

Vacuum drying

Powder

Ti ore: Rutile
Flux: CaCl$_2$
Binder: Collodion

Flux: CaCl$_2$
Binder: Collodion

FeCl$_x$

Ti ore + flux

TiO$_2$ feed in flux

Ti + CaO + Ca

CaCl$_2$

Waste solution

Ti powder
Reduction experiment in PRP

Schematic illustration of the experimental apparatus for the reduction experiment.

\[
\text{TiO}_2 \ (s, \text{ in feed preform}) + \text{Ca} \ (g) \rightarrow \text{Ti} \ (s) + \text{CaO} \ (s, \text{ in flux})
\]
Experimental apparatus

Left: Arrangement of stainless steel net and holder tentatively installed in transparent container; Right: Apparatus parts and materials used in reduction experiment before assembly.
## Experiment conditions

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mass of sample, $w_i / g$</th>
<th>Cationic molar ratio, $R_{\text{Cat.}/\text{Ti}}$</th>
<th>Calcination</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Flux</td>
<td>Binder</td>
<td>Additive</td>
</tr>
<tr>
<td>A</td>
<td>Ti ore&lt;sup&gt;a&lt;/sup&gt; 7.74</td>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt; 2.52</td>
<td>Collodion 5.58</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>6.26</td>
<td>1.74</td>
<td>4.26</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>5.65</td>
<td>2.35</td>
<td>5.79</td>
<td>0.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Natural rutile ore produced in South Africa after pulverization.

<sup>b</sup> Cationic molar ratio, $R_{\text{Cat.}/\text{Ti}} = N_{\text{Cat.}} / N_{\text{Ti}}$, where $N_{\text{Cat.}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that of titanium, respectively.

Fe removal: $\text{FeO}_x (s, \text{in Ti ore}) + \text{MCl}_y (g, l) \rightarrow \text{FeCl}_2 (g) + \text{MO}_z$

Reduction: $\text{TiO}_2 (s) + \text{Ca} (g) \rightarrow \text{Ti} (s) + \text{CaO} (s)$
Results of PRP (1): Images

Exp. A, Cationic molar ratio, $R_{\text{Cat.}/\text{Ti}} = 0.2$

(a) Fabricated feed preform

(b) After calcination

Ti ore + flux

(b) TiO$_2$ feed in flux

(c) After reduction

(d) After leaching

Ti + CaO + Ca

Ti powder
Exp. A, Cationic molar ratio, $R_{\text{Cat.}/\text{Ti}} = 0.2$

After fabrication:
$\text{TiO}_2 + \text{CaCl}_2 + \text{CaCl}_2(\text{H}_2\text{O})_4$

After Calcination:
$\text{TiO}_2 + \text{CaCl}_2 + \text{CaCl}_2(\text{H}_2\text{O})_4$

After reduction:
$\text{Ti} + \text{CaO} + \text{Ca}$

After leaching:
$\text{Ti}$

Metallic Ti powder was successfully produced “directly” from “natural titanium ore” by the PRP.
Results of PRP (3): XRD-2

Exp. B, Cationic molar ratio, $R_{\text{Cat./Ti}} = 0.2$, Carbon powder: 0.2 g

After fabrication:
$\text{TiO}_2$ (+ $\text{CaCl}_2 + \text{CaCl}_2(\text{H}_2\text{O})_4$)

After Calcination:
$\text{TiO}_2 + \text{CaTiO}_3$ (+ $\text{CaCl}_2 + \text{CaCl}_2(\text{H}_2\text{O})_4$)

After reduction:
$\text{Ti} + \text{CaO} + \text{Ca}$

After leaching:
$\text{Ti}$

The generation of $\text{CaTiO}_3$ was considered to be beneficial for the iron removal.
Results of PRP (4): XRF

Exp. B, Cationic molar ratio, $R_{\text{Cat./Ti}} = 0.2$, Carbon powder: 0.2 g

Analytical results of the samples in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of element $i$, $C_i$ (mass%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Ti ore$^a$</td>
<td>1.01</td>
</tr>
<tr>
<td>Preform</td>
<td>0.50</td>
</tr>
<tr>
<td>After calcination</td>
<td>0.08</td>
</tr>
<tr>
<td>After reduction</td>
<td>0.02</td>
</tr>
<tr>
<td>After leaching</td>
<td>0.56</td>
</tr>
</tbody>
</table>

$^a$ : Natural rutile ore produced in South Africa after pulverization.

$^b$ : Determined by X-ray fluorescence analysis, and the value excludes carbon and gaseous elements.

**Iron removal ratio: 90%**

→ The ratio is higher than the iron removal ratio of 56% in the previous experiment, in which carbon powder was not introduced in the preform.

**Purity of Ti powder: 98.23%**

Iron removal ratio: $\left( \frac{C_{\text{Fe, Bef.}}}{C_{\text{Fe, Bef.}}} - \frac{C_{\text{Fe, Aft.}}}{C_{\text{Ti, Aft.}}} \right) / \left( C_{\text{Fe, Bef.}} / C_{\text{Ti, Bef.}} \right)$
Results of PRP (5): SEM images

Exp. C, Cationic molar ratio, $R_{\text{Cat./Ti}} = 0.3$

(a) Fabricated feed preform

(b) After calcination

(c) After reduction

(d) After leaching
Results of PRP (6): Comparison of the SEM images

Exp. B, Cationic molar ratio, $R_{\text{Cat./Ti}} = 0.2$, Carbon powder: 0.2 g

Exp. C, Cationic molar ratio, $R_{\text{Cat./Ti}} = 0.3$, Carbon powder: 0.2 g

Cationic molar ratio, $R_{\text{Cat./Ti}} = \frac{N_{\text{Cat.}}}{N_{\text{Ti}}}$, where $N_{\text{Cat.}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that of titanium, respectively.
Results of PRP (7): Composition and yields of the obtained Ti product

Exp. B and C

Analytical results of the titanium samples obtained after leaching.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Cationic molar ratio, $R_{\text{Cat/Ti}}$</th>
<th>Concentration of element $i$ in obtained Ti powder, $C_i$ (mass %)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ti</td>
<td>Fe</td>
</tr>
<tr>
<td>B</td>
<td>0.2</td>
<td>98.23</td>
<td>0.23</td>
</tr>
<tr>
<td>C</td>
<td>0.3</td>
<td>98.44</td>
<td>0.14</td>
</tr>
</tbody>
</table>

- a Natural rutile ore produced in South Africa after pulverization.
- b Cationic molar ratio, $R_{\text{Cat/Ti}} = \frac{N_{\text{Cat.}}}{N_{\text{Ti}}}$, where $N_{\text{Cat.}}$ and $N_{\text{Ti}}$ are mole amount of cation in flux and that of titanium, respectively.

Still high for practical application, but will be improved.

Loss occurred mainly at leaching process.
Results of PRP: SEM images

Exp. C-7, Cationic molar ratio, $R_{\text{Cat./Ti}} = 0.3$ (UGI)

(a) Fabricated feed preform

(b) After calcination

(c) After reduction

(d) After leaching
### Experimental results: XRD, SEM images, and XRF

Exp. B, Cationic molar ratio, $R_{\text{Cat}}/\text{Ti.} = 0.2$, Carbon powder: 0.2 g

<table>
<thead>
<tr>
<th>Step</th>
<th>XRF analysis (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>(a)</td>
<td>67.64</td>
</tr>
<tr>
<td>After fabrication</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>65.99</td>
</tr>
<tr>
<td>After calcination</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>18.79</td>
</tr>
<tr>
<td>After reduction</td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>98.23</td>
</tr>
<tr>
<td>After leaching</td>
<td></td>
</tr>
</tbody>
</table>

Iron removal ratio is 90%.

Iron removal ratio: $\left(\frac{C_{\text{Fe, Bef.}}/C_{\text{Ti, Bef.}}}{C_{\text{Fe, Aft.}}/C_{\text{Ti, Aft.}}}\right)$.
**Experimental results: XRD, SEM images, and XRF**

Exp. D, Cationic molar ratio, $R_{\text{Cat.}} = 0.3$, Carbon powder: 0.2 g

<table>
<thead>
<tr>
<th>Step</th>
<th>XRF analysis (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>(a) After fabrication</td>
<td>46.11</td>
</tr>
<tr>
<td>(b) After calcination</td>
<td>49.63</td>
</tr>
<tr>
<td>(c) After reduction</td>
<td>19.98</td>
</tr>
<tr>
<td>(d) After leaching</td>
<td>98.44</td>
</tr>
</tbody>
</table>

Iron removal ratio is 65%.

Iron removal ratio:
\[
\left( \frac{C_{\text{Fe, Bef.}}}{C_{\text{Ti, Bef.}}} - \frac{C_{\text{Fe, Aft.}}}{C_{\text{Ti, Aft.}}} \right) / \left( \frac{C_{\text{Fe, Bef.}}}{C_{\text{Ti, Bef.}}} \right)
\]
Summary on Ti powder production by PRP

1. Metallic Ti powder with 98% purity up and coral-like structure was obtained directly from natural Ti ore (rutile ore) using Ca vapor by PRP.

2. Iron can be removed from the rutile ore in the preform after calcination.

3. Iron removal ratio was enhanced by introducing C powder into the preform.

4. Generation of CaTiO$_3$ was considered to be beneficial for removing iron from Ti ore.

(Recently, a technical paper on this subject was submitted to Metallurgical and Materials Transactions B.)
Summary on this study

1. Thermodynamic analysis was carried out.

2. Iron was successfully removed from the low-grade Ti ore by selective chlorination using metal chlorides.
   \[
   \text{FeO}_x (\text{FeTiO}_x, s) + \text{HCl} (g) \rightarrow \text{FeCl}_2 (l, g) + \text{H}_2\text{O} (g) \\
   \text{FeO}_x (\text{FeTiO}_x, s) + \text{CaCl}_2 (l) \rightarrow \text{FeCl}_2 (l, g) + \text{\overline{CaO}} (\text{CaTiO}_x, s)
   \]

3. The feasibility of the new recycling process of chlorine in the chloride waste by metallic Ti is demonstrated.
   \[
   \text{Ti} (s) + \text{FeCl}_2 (s, l) \rightarrow \text{TiCl}_4 (g) + \text{Fe} (s)
   \]

4. Metallic Ti powder with purity in excess of 98% and coral-like structure was obtained directly from rutile ore by PRP. It is demonstrated that PRP is suitable for producing high purity titanium powder directly from titanium ore.
   \[
   \text{TiO}_2 (s, \text{in feed preform}) + \text{Ca} (g) \rightarrow \text{Ti} (s, \text{powder}) + \text{CaO} (s, \text{flux})
   \]
Ultimate objective of this study

Establishing an innovative process for producing high-purity Ti powder with low-cost.

Ti Ore    Ti powder