Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

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Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

1. Introduction
   • Background
   • Previous research works
   • Purpose of this study
2. Experimental
3. Experimental results
4. Summary and future works
Titanium?

Features of Titanium

1. Light and high-strength
2. Corrosion resistance
3. Biocompatibility
4. 9th most abundant element in the earth’s crust

Ocean industry

The JAPAN TITANIUM SOCIETY

Implant

http://www.atlantadentalimplants.com/

Buildings

TMinato-Machi River Place (Osaka Japan)

http://www.city.osaka.jp/
Current status of titanium production

(a) Production of titanium sponge in the world (2003)

- Japan: 18.5 kt (28% share)
- USA: 8 kt
- Russia: 26 kt
- Kazakhstan: 9 kt
- China: 4 kt
- Total: 65.5 kt

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

Japan has about 30% world market share, and its titanium industry is growing steadily.
### Comparison with common metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Iron (Fe)</th>
<th>Aluminum (Al)</th>
<th>Titanium (Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Fe</td>
<td>Al</td>
<td>Ti</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>1809</td>
<td>933</td>
<td>1939</td>
</tr>
<tr>
<td>Density (g/cm³@298 K)</td>
<td>7.9</td>
<td>2.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Specific strength ((kgf/mm²)/(g/cm³))</td>
<td>4~7</td>
<td>3~6</td>
<td>8~10</td>
</tr>
<tr>
<td>Clarke No.</td>
<td>4</td>
<td>3</td>
<td>9</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@2003)</td>
<td>9.6 x 10⁸</td>
<td>2.2 x 10⁷</td>
<td>6.6 x 10⁴</td>
</tr>
</tbody>
</table>

Production volume of metallic Ti is substantially small compared to common metals.
Kroll process

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

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 Ti obtainable

The critical disadvantage:
- Batch type process
- Labor and energy consuming
- Slow production speed
  \( \rightarrow \) Low productivity
Various reduction processes for titanium oxides

(a) FFC process (Fray et al.)

(b) OS process (Ono & Suzuki)

TiO₂ powder → Ca

CaCl₂ molten salt

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

Current monitor / controller

TiO₂ powder

CaCl₂ molten salt

(d) Preform reduction process (PRP)

Carbon anode

TiO₂

CaCl₂-CaO molten salt

Ca-X alloy

Reductant vapor

Reductant (R = Ca, or Ca-X alloy)

Feed preform (TiO₂ feed + flux)
The purpose of this study

Development of a new smelting process for producing high purity titanium.

- High productivity, low cost process has to be developed for replacing the Kroll process

Preform reduction process (PRP)

TiO₂ (s, feed preform) + Ca (g) → Ti (s, powder) + CaO (s, flux)
Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

1. Introduction
2. Experimental
   - Concept of PRP
   - Flowchart of this study
   - PRP experiment with no carbon powder
   - PRP experiment with carbon powder
3. Experimental results
4. Summary and future works
Preform Reduction Process (PRP)?

Feeding preform (TiO$_2$ feed + flux) → Reductant vapor

Reductant (R = Ca, or Ca-X alloy)

Advantages of Preform Reduction Process:
- "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 Preform Reduction Process:
- Leaching process is required
- Calcium production and control of calcium vapor is difficult

TiO$_2$ (s, feed preform) + Ca (g) → Ti (s, powder) + CaO (s, flux)
Fig. 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
Vapor pressure of some selected metals and chlorides

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 or TiO₂ in the PRP.

Fig. Vapor pressure of selected metals and chlorides.
Starting materials

Previous study: Artificial feed materials

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Upgraded ilmenite (India)</th>
<th>Titanium Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Or</td>
<td>De-ionized ilmenite ore</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Rutile ore (South Africa)</th>
<th>XRF analysis (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRF analysis</td>
<td>Ti</td>
</tr>
<tr>
<td></td>
<td>96.82</td>
</tr>
</tbody>
</table>

So far, it was difficult to produce high-purity Ti directly from natural Ti ore!
Experimental procedure

<table>
<thead>
<tr>
<th>Ti ore</th>
<th>Flux</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing</td>
<td>Slurry</td>
<td></td>
</tr>
</tbody>
</table>

- **Preform fabrication**
  - Rutile+CaCl₂+Binder
  - $T$: Room temp.; $t'$: 6 hr
  - e.g. 40mm × 20mm × 8mm

- **Feed preform**
  - $T$: 1273 K; $t'$: 1 hr~2hr
  - Calcination/iron removal
  - $T$: 1273 K, $t'$: 6 hr~9 hr
  - Reduction
  - Calcium vapor
  - Reduced preform
  - $T$: RT
  - $50\%$ CH₃COOH aq., $t'$: 6 hr
  - $20\%$ HCl aq., $t'$: 1 hr
  - **Leaching**
  - **Vacuum drying**
  - **Powder**

Ti ore: Rutile
Flux: CaCl₂
Binder: Collodion

Ti ore + flux
TiO₂ feed in flux
Ti + CaO + Ca
Waste solution
Ti powder
Experimental apparatus for the reduction process in PRP

Fig. Schematic illustration of the experimental apparatus for the reduction experiment.

Fig. Arrangement of stainless steel net and holder tentatively installed in transparent container.
### Experimental conditions

#### Table: Experimental conditions in this study.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mass of sample, $w_i$ / g</th>
<th>Cationic Molar ratio, $R_{\text{Cat.}} / Ti$</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\textsuperscript{a}</td>
<td>CaCl\textsubscript{2}</td>
<td>Collodion</td>
<td>Carbon powder</td>
</tr>
<tr>
<td>B</td>
<td>6.65</td>
<td>3.86</td>
<td>6.01</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>6.26</td>
<td>1.74</td>
<td>4.26</td>
<td>0.2</td>
</tr>
<tr>
<td>D</td>
<td>5.65</td>
<td>2.35</td>
<td>5.79</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Natural rutile ore produced in South Africa after pulverization.

\textsuperscript{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.

---

Fe removal  
Ti powder production
Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

1. Introduction
2. Experimental

3. Experimental results
   ● Analytical data by XRD, XRF, and SEM

4. Summary and future works
Experimental results: Images and XRD

Exp. A, Cationic molar ratio, $R = 0.2$

(a) Fabricated feed preform
(b) After calcination
(c) After reduction
(d) After leaching

Ti ore + flux
TiO$_2$ feed in flux
Ti + CaO + Ca
Ti powder

XRD patterns

TiO$_2$ + CaCl$_2$ + CaCl$_2$(H$_2$O)$_4$
TiO$_2$ + CaCl$_2$ + CaCl$_2$(H$_2$O)$_4$
Ti + CaO + Ca
Ti
Experimental results: SEM images and XRF

Exp. B, Cationic molar ratio, \( R = 0.3 \)

<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>68.00</td>
</tr>
<tr>
<td>(b)</td>
<td>60.68</td>
</tr>
<tr>
<td>(c)</td>
<td>17.74</td>
</tr>
<tr>
<td>(d)</td>
<td>99.10</td>
</tr>
</tbody>
</table>

Iron removal ratio is 56 %
Experimental results: XRD, SEM images, and XRF

Exp. C, Cationic molar ratio, $R = 0.2$, 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) After fabrication</td>
<td>67.64</td>
</tr>
<tr>
<td>(b) After calcination</td>
<td>65.99</td>
</tr>
<tr>
<td>(c) After reduction</td>
<td>18.79</td>
</tr>
<tr>
<td>(d) After leaching</td>
<td>98.23</td>
</tr>
</tbody>
</table>

Iron removal ratio:

\[
\frac{C_{Fe, \text{Aft.}}/C_{Ti, \text{Aft.}} - C_{Fe, \text{Bef.}}/C_{Ti, \text{Bef.}}}{C_{Fe, \text{Bef.}}/C_{Ti, \text{Bef.}}}
\]
Experimental results: XRD, SEM images, and XRF

Exp. D, Cationic molar ratio, $R = 0.3$, 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:

$$\frac{(C_{Fe, Bef.}/C_{Ti, Bef.} - C_{Fe, Aft.}/C_{Ti, Aft.})}{(C_{Fe, Bef.}/C_{Ti, Bef.})}$$

Iron removal ratio is 65%. 

Experimental results: XRD, SEM images, and XRF
### Composition and yields of the obtained Ti product

#### Exp. C and D

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Cationic molar ratio, $R_{\text{Cat.}}/\text{Ti}$</th>
<th>Concentration of element $i$ in obtained Ti powder, $C_i$ (mass %)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.2</td>
<td>Ti: 98.23, Fe: 0.23, Al: 0.56, Ca: 0.98, Cl: (0.00)</td>
<td>79.02</td>
</tr>
<tr>
<td>D</td>
<td>0.3</td>
<td>Ti: 98.44, Fe: 0.14, Al: 0.73, Ca: 0.68, Cl: (0.00)</td>
<td>87.74</td>
</tr>
</tbody>
</table>

**Table** Analytical results of the titanium samples obtained after leaching.

- **Exp. C** and **D**

- **Natural rutile ore produced in South Africa after pulverization.**

- **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.**

- **Still high for practical application, but will be improved.**

- **Loss occurred mainly at leaching process.**
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Summary

1. Iron was successfully removed by selective chlorination in the calcination step, and 90 % of iron was removed.

2. When carbon powder is added to the preform, the effect of iron removal became more efficient. Titanium powder with 98 mass % purity was obtained with the yield of 88 %.

3. High-purity metallic titanium powder (99 mass % up) was obtained directly from natural titanium ore (rutile ore) by Preform Reduction Process (PRP).
Future Works

1. Development of more effective method for removing iron directly from titanium ore.

2. Development of efficient recycling system of CaCl₂ flux, and residual Ca reductant.

The ultimate object:
→ establishing an innovative process for producing high-purity titanium powder with low-cost.
Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

- **Ti ore** → **Flux** → **Binder**
  - Mixing
  - Slurry
  - Preform fabrication
  - Feed preform
  - Calcination/iron removal
  - Sintered feed preform
  - Reduction
  - Reduced preform
  - Leaching
  - Vacuum drying
  - Powder

### Process Details

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

### Titania Feed Preparation

- Rutile + CaCl₂ + Binder
- Room temp.; $t$: 6 hr
- E.g. 40mm $\times$ 20mm $\times$ 8mm

### Reduction Process

- 1273 K; $t$: 1 hr ~ 2 hr

### Leaching

- 50% CH₃COOH aq., $t$: 6 hr
- 20% HCl aq., $t$: 1 hr

### Final Powder Characteristics

- 0.8~1.4 mass % Fe
- 90% Fe removal
- 98% purity
- ~0.13 mass % Fe
- 98 mass % purity
- 0.14 mass % Fe
- 88% yield
Acknowledgments

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

The tenth most abundant element

Exhausting element...
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)
Shipments of titanium mill product in various field’s application in China (2004).
The Kroll process

**Carbo-chlorination**

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

**Distillation**

- Crude TiCl₄
- CO₂
- FeCl₅, AlCl₃

**Reduction**

- Pure TiCl₄
- Other compounds
- Mg

**Electrolysis**

- MgCl₂

**The essential advantage:**
High-purity titanium available.

**The critical disadvantage:**
Low productivity.

**Chemical Reaction:**

\[
\text{TiCl}_4(g) + 2 \text{Mg}(l) \rightarrow \text{Ti}(s) + 2 \text{MgCl}_2(l)
\]
Comparison of various new processes for titanium production

(a) FFC process

(b) OS process

(c) EMR / MSE process (Oxide system)

Fig. Comparison of various reduction processes of titanium oxide in molten calcium chloride medium.
Flowchart of the Beacher process.

Flowchart of the Beacher process.

Ilmenite  Coal (low ash)  Air

Reduction (in kiln)

Reduced ore  Gas + particle  Particle

Screen

-1 mm  +1 mm

Mag. separator

Reduced ilmenite  NH₄Cl  Air

Leaching


Acid Leaching

TiO₂

Filtering / Drying

TiO₂ (Synthetic rutile)

TiO₂  92~93%; TiFe  2.0~3.5%

Flowchart of the Beacher process.
Flowchart of the Benilite process.
Features of reductant and feed materials in metallothermic reduction process.

<table>
<thead>
<tr>
<th></th>
<th>TiCl₄</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>©</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>Possible to remove Mg and MgCl₂ by distillation.</td>
<td>Impossible to remove oxygen</td>
</tr>
<tr>
<td></td>
<td>Possible to efficiently eletrosis MgCl₂</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>□</td>
<td>×</td>
</tr>
<tr>
<td></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>△</td>
<td>□</td>
</tr>
<tr>
<td></td>
<td>High enegy loss</td>
<td>Difficult to purity control</td>
</tr>
<tr>
<td></td>
<td>Difficult to remove Ca or CaCl₂</td>
<td>Difficult to remove Ca or CaCl₂</td>
</tr>
<tr>
<td></td>
<td>? Cost of the reductant production</td>
<td>? Cost of the reductant production</td>
</tr>
<tr>
<td></td>
<td>↑ Process with strong resistace to Oxygen</td>
<td></td>
</tr>
</tbody>
</table>
Chlorine cycle in the Kroll process

- Chlorine in the Kroll process is recycled, but the generation of chloride waste causes chlorine loss in the process.
- Additional Cl₂ supply to compensate for chlorine loss.

1. Carbo-chlorination
   - Ti ore
   - C
   - TiCl₄
   - COₓ
   - Chloride wastes

2. Reduction
   - Mg
   - MgCl₂
   - Ti

3. Electrolysis
   - Cl₂
   - Mg
Upgrading Ti ore for minimizing chloride wastes

Problems:
When low-grade ore is used, a large amount of chloride wastes (e.g., FeClₓ) are generated in the Kroll process. → Disposal cost of chloride wastes → Environmental issues → Causes chlorine loss in the process

Current:
Currently expensive upgraded ore is used for reducing chloride waste and environmental burden.
Table  Gibbs energy change of formation and reaction in the Fe-Ti-O system.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Gibbs energy change, $\Delta G_r$ (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe} (s) + 0.5 \text{O}_2 (g) = \text{FeO} (s)$</td>
<td>-200.709, -194.362, -187.999, -189.717</td>
<td>1</td>
</tr>
<tr>
<td>$\text{Ti} (s) + \text{O}_2 (g) = \text{TiO}_2 (s)$</td>
<td>-744.912, -727.229, -709.392, -714.208</td>
<td>1</td>
</tr>
<tr>
<td>$\text{Fe} (s) + \text{Ti} (s) + 1.5 \text{O}_2 (g) = \text{FeTiO}_3 (s)$</td>
<td>-956.608, -931.690, -906.600, -913.374</td>
<td>1</td>
</tr>
<tr>
<td>$2 \text{Fe} (s) + \text{Ti} (s) + 2 \text{O}_2 (g) = 2\text{Fe}_2\text{TiO}_4 (s)$</td>
<td>-1164.697, -1133.483, -1102.214, -1110.66</td>
<td>1</td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + \text{FeO} (s) = \text{FeTiO}_3 (s)$</td>
<td>-10.987, -10.099, -9.209, -9.449</td>
<td>1</td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + 2 \text{FeO} (s) = 2\text{Fe}_2\text{TiO}_4 (s)$</td>
<td>-26.462, -25.05, -24.638, -24.749</td>
<td>3</td>
</tr>
</tbody>
</table>

References

$\text{TiO}_x + \text{FeO} = \text{Ti}_x\text{Fe}_y\text{O}_z$

$\Delta G_r = -30 \sim -9 \text{ kJ / mol}$
Table Starting materials used in this study.

<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.
### Table Titanium ore used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of element ( i ), ( C_i ) (mass%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Si</td>
</tr>
<tr>
<td>UGI&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95.47</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>95.85</td>
<td>0.37</td>
</tr>
<tr>
<td>Rutile&lt;sup&gt;c&lt;/sup&gt;</td>
<td>93.10</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>93.55</td>
<td>1.05</td>
</tr>
</tbody>
</table>

---

<sup>a</sup> Determined by X-ray fluorescence analysis (XRF).

<sup>b</sup> Up-graded ilmenite produced in India by the Beacher process.

<sup>c</sup> Natural rutile ore produced in South Africa.

<sup>d</sup> Not detected. Below detection limit of XRF (<0.01%).
Table 3-1 Analytical results of obtained titanium powder by preform reduction process using UGP.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Flux</th>
<th>Reduction molar ratio, $R_{\text{Cat.}/\text{Ti}}$</th>
<th>Reduction temp., $T_{\text{red}} / \text{K}$</th>
<th>Oxgen, $C_{\text{O}}$ (mass%)</th>
<th>Aluminum, $C_{\text{Al}}$ (mass%)</th>
<th>Calcium, $C_{\text{Ca}}$ (mass%)</th>
<th>Titanium, $C_{\text{Ti}}$ (mass%)</th>
<th>Iron, $C_{\text{Fe}}$ (mass%)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>CaCl$_2$</td>
<td>0.2</td>
<td>1273</td>
<td>(0.00)</td>
<td>0.40</td>
<td>0.11</td>
<td>98.94</td>
<td>0.57</td>
<td>040510_CaCl$_2$_Ca_1273_6h_11-1</td>
</tr>
<tr>
<td>A-2</td>
<td>CaCl$_2$</td>
<td>0.3</td>
<td>1273</td>
<td>(0.00)</td>
<td>0.25</td>
<td>0.12</td>
<td>99.41</td>
<td>0.22</td>
<td>040510_CaCl$_2$_Ca_1273_6h_5-2</td>
</tr>
<tr>
<td>A-3</td>
<td>CaCl$_2$</td>
<td>0.3</td>
<td>1273</td>
<td>(0.00)</td>
<td>0.17</td>
<td>0.10</td>
<td>99.24</td>
<td>0.50</td>
<td>040510_CaCl$_2$_Ca_1273_6h_6-1</td>
</tr>
<tr>
<td>A-4</td>
<td>CaCl$_2$</td>
<td>0.2</td>
<td>1273</td>
<td>0.13</td>
<td>0.13</td>
<td>0.92</td>
<td>98.58</td>
<td>0.32</td>
<td>Refer Mashimo's data$^d$.</td>
</tr>
<tr>
<td>A-5</td>
<td>CaCl$_2$</td>
<td>0.2</td>
<td>1273</td>
<td>(0.00)</td>
<td>0.19</td>
<td>0.11</td>
<td>99.70</td>
<td>0.01</td>
<td>Refer Mashimo's data$^d$.</td>
</tr>
<tr>
<td>A-6</td>
<td>CaCl$_2$</td>
<td>0.3</td>
<td>1273</td>
<td>(0.00)</td>
<td>0.24</td>
<td>0.03</td>
<td>99.60</td>
<td>0.13</td>
<td>Refer Mashimo's data$^d$.</td>
</tr>
<tr>
<td>A-7</td>
<td>CaCl$_2$</td>
<td>0.3</td>
<td>1273</td>
<td>(0.00)</td>
<td>0.19</td>
<td>0.04</td>
<td>99.71</td>
<td>0.08</td>
<td>Refer Mashimo's data$^d$.</td>
</tr>
</tbody>
</table>

a : Up-graded ilmenite produced in India by the Beacher process (See Table 2-2).

b : 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 flux and of titanium, respectively.

c : Analyzed by EDS. Values in parenthesis are listed for reference.

## Properties of TiCl$_x$

<table>
<thead>
<tr>
<th>Property</th>
<th>TiCl$_4$</th>
<th>TiCl$_3$</th>
<th>TiCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td></td>
<td><img src="image" alt="Red" /></td>
<td><img src="image" alt="Black" /></td>
</tr>
<tr>
<td>Color</td>
<td>Clear</td>
<td>Red</td>
<td>Black</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>189.7</td>
<td>154.2</td>
<td>118.8</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.70</td>
<td>No data</td>
<td>3.13</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>−24.1</td>
<td>425</td>
<td>1035</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>136.5</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Sublimation point (°C)</td>
<td>−</td>
<td>830</td>
<td>1307</td>
</tr>
<tr>
<td>$\Delta G^\circ_f$ at 800°C (kJ/mol Cl$_2$)</td>
<td>−317</td>
<td>−327</td>
<td>−344</td>
</tr>
<tr>
<td>$\Delta G^\circ_f$ at 800°C (kJ/mol Ti)</td>
<td>−637</td>
<td>−491</td>
<td>−344</td>
</tr>
<tr>
<td>Vapor pressure at 800°C (atm)</td>
<td>−</td>
<td>0.74</td>
<td>$1.2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Mechanism of iron removal (FeO$_x$ chlorination)

Fe-Cl-O system, $T = 1300$ K

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

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

□ : 
H$_2$O (g) + CaCl$_2$ (l) → 2 HCl (g) + CaO (s)
FeO$_x$ (FeTiO$_x$, s) + HCl (g) → FeCl$_x$ (l, g) + H$_2$O (g)

□ : 
FeO$_x$ (FeTiO$_x$, s) + CaCl$_2$ (l) → FeCl$_x$ (g) + CaO (CaTiO$_x$, s)
a$_{CaO}<<1$

FeO$_x$ can be chlorinated using CaCl$_2$ + H$_2$O.
Fig. Chemical potential diagram of the Ti-Cl-O system at 1300 K.

Mechanism of iron removal (TiO$_x$ chlorination)

TiO$_x$ can not be chlorinated using CaCl$_2$, nor CaCl$_2$+H$_2$O.
Mechanism of iron removal Ti ore chlorination

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

Fig. 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$_x$ ($g$) $\uparrow$ + H$_2$O ($g$)  
FeO$_x$ (FeTiO$_x$, $s$) + CaCl$_2$ ($l$)  
$\rightarrow$ FeCl$_x$ ($g$) $\uparrow$ + CaO (CaTiO$_x$, $s$)  

$\alpha_{\text{CaO}} << 1$

FeO$_x$ can be chlorinated using CaCl$_2$+H$_2$O. TiO$_x$ can not be chlorinated using CaCl$_2$, nor CaCl$_2$+H$_2$O.
Mechanism of iron removal Ti ore chlorination

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

FeO<sub>x</sub> (FeTiO<sub>x</sub>, s) + HCl (g) → FeCl<sub>x</sub> (g) ↑ + H<sub>2</sub>O (g)

FeO<sub>x</sub> (FeTiO<sub>x</sub>, s) + CaCl<sub>2</sub> (l) → FeCl<sub>x</sub> (g) ↑ + CaO (CaTiO<sub>x</sub>, s)

FeO<sub>x</sub> can be chlorinated using CaCl<sub>2</sub>+H<sub>2</sub>O. TiO<sub>x</sub> can not be chlorinated using CaCl<sub>2</sub>, nor CaCl<sub>2</sub>+H<sub>2</sub>O.

FeCl<sub>3</sub> (g), FeCl<sub>2</sub> (g), H<sub>2</sub>O (g), HCl (g) eq.

FeO<sub>x</sub> can be chlorinated using CaCl<sub>2</sub>+H<sub>2</sub>O. TiO<sub>x</sub> can not be chlorinated using CaCl<sub>2</sub>, nor CaCl<sub>2</sub>+H<sub>2</sub>O.
Temperature Dependence of vapor pressure of some chlorides, e.g. Mg and Ca

Vapor pressure of several chemical species. [Ref. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]
Experimental results: XRD, SEM images, and XRF

Exp. D, Cationic molar ratio, R = 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>56.83</td>
</tr>
<tr>
<td>(b) After calcination</td>
<td>49.51</td>
</tr>
<tr>
<td>(c) After reduction</td>
<td>20.56</td>
</tr>
<tr>
<td>(d) After leaching</td>
<td>98.00</td>
</tr>
</tbody>
</table>

Iron removal ratio is 61%
Composition and yields of the obtained Ti product

Exp. C and D

Table  Analytical results of the titanium samples obtained after leaching.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Cationic molar ratio</th>
<th>Concentration of element $i$ in obtained Ti powder, $C_i$ (mass %)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{\text{Ca/Ti}}$</td>
<td>Ti</td>
<td>Fe</td>
</tr>
<tr>
<td>C</td>
<td>0.2</td>
<td>98.23</td>
<td>0.23</td>
</tr>
<tr>
<td>D</td>
<td>0.3</td>
<td>98.00</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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

1) Fabricated feed preform

(b) After calcination

(c) After reduction

(d) After leaching

Figure 7: (a) Fabricated platy feed preform. (Flux: CaCl₂, Binder: Collodion)
(b) After calcination. (Temp.: $T_{\text{cal.}} = 1273$ K, holding time: $t_{\text{cal.}} = 1$ h.)
(c) After reduction. (Temp.: $T_{\text{red.}} = 1273$ K, holding time: $t_{\text{red.}} = 6$ h.)
(d) Titanium powder obtained after leaching. Ito-san
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image and EDS
(E_1_1_2)
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image and EDS
(E_2_1_2_rutile)
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image and EDS
(E_5_1_2_ilmenite)

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Fe</th>
<th>Ca</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>29.03</td>
<td>0.27</td>
<td>28.83</td>
<td>0.84</td>
<td>41.04</td>
</tr>
</tbody>
</table>

CaTiO$_3$
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image
(B_2_1_1_rutile)
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image
(E_6_1_1_ilmenite)

\[ \text{TiO}_2 \]
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image
(B_1_1_2_rutile?)
Reduction Experimental

Schematic illustration of the experimental apparatus for reduction.

Materials: Preform (Mixture of Ti ore, CaCl₂ and Binder)
T: 1273 K
t': 6 h
Reductant: Ca shot
## Starting Materials

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Concentration of element $i$, $C_i$ (mass%$^a$)</th>
<th>XRF file name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Si</td>
</tr>
<tr>
<td>ilmenaite$^b$</td>
<td>1.60</td>
<td>2.30</td>
</tr>
<tr>
<td>ilmenaite$^c$</td>
<td>0.75</td>
<td>2.19</td>
</tr>
<tr>
<td>Haiyan's analysis</td>
<td>0.07</td>
<td>0.44</td>
</tr>
<tr>
<td>UGI$^d$</td>
<td>0.05</td>
<td>0.42</td>
</tr>
<tr>
<td>UGI$^e$</td>
<td>0.04</td>
<td>0.36</td>
</tr>
</tbody>
</table>

$^a$: Value determined by XRF analysis, n.d. notes not detected (below 0.01 mass%).

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

$^c$: Natural ilmenite ore produced in Viet Nam.

$^d$: Up-graded ilmenite by the Beacher process. The ore was produced in Australia.

$^e$: Up-graded ilmenite by the Benilite process. The ore was produced in India.