Iron Removal from Titanium Ore by Electrochemical Method

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Introduction

**Feature of titanium**
- Lightweight and high-strength
- Corrosion resistant
- Biocompatibility
- Some titanium alloys: shape-memory effect, super elasticity

**Application**
- Aircraft
- Spacecraft
- Chemical plant
- Implant
- Artificial bone etc.

**The Kroll process**: Current Ti production process

1. **Chlorination**
   \[ \text{Ti ore} + C + 2 \text{Cl}_2 \rightarrow \text{TiCl}_4 (+ \text{FeCl}_x) + \text{CO}_2 \]

2. **Reduction**
   \[ \text{TiCl}_4 + 2 \text{Mg} \rightarrow \text{Ti} + 2 \text{MgCl}_2 \]

3. **Electrolysis**
   \[ \text{MgCl}_2 \rightarrow \text{Mg} + \text{Cl}_2 \]

**Diagram**:
- Mg & TiCl\(_4\) feed port
- Reaction container
- Sponge titanium
- MgCl\(_2\)
2. Chlorine circulation in the Kroll process can be improved.

3. This process can also be applied to the new Ti production processes, e.g., the direct electrochemical reduction of TiO₂.

Advantages:

1. Material cost can be reduced by using low grade ore.

2. Chlorine circulation in the Kroll process can be improved.

3. This process can also be applied to the new Ti production processes, e.g., the direct electrochemical reduction of TiO₂.
The selective-chlorination of Ti ore by MgCl₂ or CaCl₂ is found to be feasible.

FeOₓ (s, in Ti ore) + MgCl₂ (s, l) → FeClₓ (l, g) + MgO (s)

CaCl₂ (s, l) + H₂O (g) → HCl (g) + CaO (s)

FeOₓ (s, in Ti ore) + HCl (g) → FeClₓ (l, g) + H₂O (g)

T = 973 ~ 1373 K

Objective of this study

1. Thermodynamic analysis of selective chlorination
2. Fundamental experiments of selective chlorination by electrochemical methods
3. Reduction experiment for the sample obtained by selective chlorination

Chain of reactions:

- Low grade Ti ore \( \xrightarrow{(\text{FeTiO}_x)} \) Fe removal by selective chlorination
- \( \text{TiO}_2 + \text{flux} \) \( \xrightarrow{} \) Direct reduction of TiO\(_2\) obtained after Fe removal
- Ti powder

Application of electrochemical method using molten salt
Thermodynamic analysis (Ti ore chlorination)

The selective chlorination of Ti ore by controlling chlorine partial pressure may be possible using an electrochemical technique.

**Fig.** Chemical potential diagram for Fe-Cl-O and Ti-Cl-O systems at 1100 K.

Ti ore: $\text{FeTi}_x\text{O}_y$

For simplicity, assuming mixture of $\text{TiO}_x$ and $\text{FeO}_x$

\[
\text{TiO}_2 \rightarrow \text{Stable} \quad \text{FeO}_x \rightarrow \text{FeCl}_x (g)
\]

The selective chlorination of Ti ore by controlling chlorine partial pressure may be possible using an electrochemical technique.
Chlorination by increased Cl₂ potential

Electrolysis

Cathode:

\[
\begin{align*}
\text{Fe}^{n+} + n \text{e}^- & \rightarrow \text{Fe} \\
\text{Ca}^{2+} + 2 \text{e}^- & \rightarrow \text{Ca}
\end{align*}
\]

Anode:

\[2 \text{Cl}^- (\text{in CaCl}_2) \rightarrow \text{Cl}_2 + 2 \text{e}^-\]

\[\text{FeO}_x + \text{Cl}_2 \rightarrow \text{FeCl}_x \uparrow + \text{O}^{2-}\]

Chlorine chemical potential at anode in molten CaCl₂ can be increased electrochemically.
Theoretical decomposition voltage

Table  Standard Gibbs energy of decomposition and theoretical voltage of that in several chemical species at 1100 K.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta G^\circ / \text{kJ}^a$</th>
<th>$\Delta E^\circ / \text{V}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CaCl}_2 (l) = \text{Ca} (l) + \text{Cl}_2 (g)$</td>
<td>629</td>
<td>3.26</td>
</tr>
<tr>
<td>$\text{FeO} (s) = \text{Fe} (s) + \frac{1}{2} \text{O}_2 (g)$</td>
<td>201</td>
<td>1.04</td>
</tr>
<tr>
<td>$\text{FeO} (s) + \frac{1}{2} \text{C} (s) = \text{Fe} (s) + \frac{1}{2} \text{CO}_2 (g)$</td>
<td>3</td>
<td>0.02</td>
</tr>
<tr>
<td>$\text{FeO} (s) + \text{CaCl}_2 (l) + \text{C} (s) = \text{FeCl}_2 (l) + \text{CO} (g) + \text{Ca} (l)$</td>
<td>409</td>
<td>2.23</td>
</tr>
<tr>
<td>$\text{FeTiO}_3 (s) + \text{CaCl}_2 (l) + \frac{1}{2} \text{C} (s)$</td>
<td>438</td>
<td>2.34</td>
</tr>
<tr>
<td>$\quad = \text{TiO}_2 (s) + \text{FeCl}_2 (l) + \text{Ca} (l) + \frac{1}{2} \text{CO}_2 (g)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Under a certain condition, selective chlorination of Fe in Ti ore may proceed below theoretical decomposition voltage of CaCl$_2$. 
Iron removal by selective chlorination using electrochemical method

Low grade Ti ore (FeTiOₓ)

Fe removal by selective chlorination

TiO₂ + flux

Direct reduction of TiO₂ obtained after Fe removal

Ti powder
Experimental apparatus

(a) Reaction chamber

(b) Reaction cell

- Potential lead (Nickel wire)
- Stainless steel tube (Electrode)
- Ar inlet
- Rubber plug
- Wheel flange
- Thermocouple
- Heater
- Mild steel crucible (Cathode)
- Graphite crucible (Anode)
- Sample
- Molten salt (CaCl₂)
- Ceramic insulator

- Support rod (Stainless steel tube)
- Air hole
- Screw (Stainless steel)
- Surface of molten salt
- Holes for molten salt diffusion
- Graphite crucible
- Sample (Ti ore, CaCl₂, etc.)
## Selective chlorination experiment

### Experimental condition:
- **Temperature:** 1100 K
- **Atmosphere:** Ar
- **Molten salt:** CaCl₂ (800 g)
- **Cathode:** Mild steel crucible (I.D. 96 mm)
- **Anode:** Carbon crucible (I.D. 17 mm)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Sample</th>
<th>Molten CaCl₂</th>
<th>Cathode</th>
<th>Anode</th>
<th>Voltage, Time, E / V, t” / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ti ore</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5, 12</td>
</tr>
<tr>
<td>B</td>
<td>Ti ore</td>
<td>0.74</td>
<td>2.17</td>
<td>—</td>
<td>1.5, 3</td>
</tr>
<tr>
<td>C</td>
<td>Ti ore</td>
<td>0.74</td>
<td>2.17</td>
<td>0.18</td>
<td>1.5, 3</td>
</tr>
<tr>
<td>D</td>
<td>—</td>
<td>1.59</td>
<td>1.27</td>
<td>—</td>
<td>1.5, 3</td>
</tr>
<tr>
<td>E</td>
<td>—</td>
<td>1.59</td>
<td>1.27</td>
<td>—</td>
<td>2.0, 3</td>
</tr>
</tbody>
</table>

### Notes:
- Low initial Fe content!
### Result of selective chlorination experiment

#### XRF analysis

Table: Analytical results of the sample obtained after electrochemical selective chlorination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of element $i, C_i$ (mass %)</th>
<th>Fe / Ti ratio, $R_{Fe/Ti}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Fe</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>42.6</td>
<td>48.7</td>
</tr>
<tr>
<td>Exp. A</td>
<td>45.7</td>
<td>21.7</td>
</tr>
<tr>
<td>Exp. B</td>
<td>47.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Exp. C</td>
<td>30.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Exp. X</td>
<td>45.1</td>
<td>5.8</td>
</tr>
<tr>
<td>UGI</td>
<td>95.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Exp. D</td>
<td>98.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Exp. E</td>
<td>96.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>VTi</th>
<th>Fe</th>
<th>Ca</th>
<th>Si</th>
<th>V</th>
<th>Fe / Ti ratio, $R_{Fe/Ti}$ (%)</th>
</tr>
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<tbody>
<tr>
<td>Exp. A</td>
<td>0.5</td>
<td>21.7</td>
<td></td>
<td></td>
<td></td>
<td>21.7</td>
</tr>
<tr>
<td>Exp. B</td>
<td>0.4</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>Exp. C</td>
<td>0.1</td>
<td>7.5</td>
<td></td>
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Fe / Ti ratio decreased from 114% to 7.2% (ilmenite), or from 2.00% to 0.18% (UGI).

94% of Fe in ilmenite and 92% of Fe in UGI was successfully removed.

a: Average of the samples obtained from the upper part and lower part of the graphite crucible.

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The 21st Rare Metal Meeting; March 10, 2006
Mixture of CaTiO₃ and TiO₂ was obtained after the Fe removal.

**XRD analysis**

Ilmenite: FeTiO₃

<table>
<thead>
<tr>
<th>Angle, 2θ (degree)</th>
<th>Ilmenite: FeTiO₃</th>
<th>:CaTiO₃</th>
<th>:TiO₂</th>
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<td></td>
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Fig. XRD pattern of the start sample and the sample obtained after the Fe removal (Exp. B).

**Discussion**

FeTiO₃ (s) + CaCl₂ (l)

→ CaTiO₃ (s) + FeClₓ (l, g)

FeTiO₃ (s) + CaCl₂ (l) + C (s)

→ TiO₂ (s) + FeClₓ (l, g) + COₓ (g) + Ca (s)

CaTiO₃ can be utilized for feed material of direct TiO₂ reduction processes (e.g. FFC, OS, EMR-MSE processes).
Low grade Ti ore
(FeTiO_x)

Fe removal by selective chlorination

TiO_2 + flux

Direct reduction of TiO_2 obtained after Fe removal

Ti powder

Direct reduction of TiO_2 after Fe removal by electrochemical method
Reduction experiment apparatus

Direct reduction by electrochemical method was applied.

Electrolysis

Cathode:
\[ \text{TiO}_2 + 4 \text{ e}^- \rightarrow \text{Ti} + 2 \text{ O}^{2-} \]

Anode:
\[ \text{C} + x \text{ O}^{2-} \rightarrow \text{CO}_x + 2x \text{ e}^- \]

Fig. Schematic illustration of experimental apparatus in this study.
Reduction experiment

Experimental condition:
Temperature: 1100 K
Atmosphere: Ar
Molten salt: CaCl₂ (800 g)
Cathode: Ti crucible (I.D. 18 mm)
Anode: Graphite rod (O.D. 3 mm)

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<tr>
<td>Exp. D</td>
<td>98.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Exp. E</td>
<td>96.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mass of element $i, w_i$ / g</th>
<th>Voltage, Time, $E/V$, $t''/h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-1</td>
<td>Ti ore</td>
<td>CaTiO₃</td>
</tr>
<tr>
<td>R-2</td>
<td>—</td>
<td>1.50</td>
</tr>
<tr>
<td>R-3</td>
<td>0.79</td>
<td>—</td>
</tr>
<tr>
<td>R-4</td>
<td>0.76</td>
<td>—</td>
</tr>
</tbody>
</table>
CaTiO$_3$ was changed into Ti$_2$O in this reduction experiment.

Reduction was incomplete in this study.
Summary

- The selective chlorination of Ti ore by using an electrochemical method was investigated, and 94% of Fe was successfully removed directly from low-grade Ti ore.

- Feasibility of Ti smelting process for producing metallic Ti directly from low-grade Ti ore was demonstrated.

Development of an industrial scale process with the purpose of producing low-cost titanium.

Low-grade Ti ore \((\text{FeTiO}_x)\)

Iron removal by selective chlorination

\(\text{TiO}_2 + \text{flux}\)

Reduction by electrochemical method

\(\text{Ti powder}\)