Selective Chlorination of Titanium Ore by Electrochemical Method

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Introduction

Features of titanium
- Light weight and high strength
- Corrosion resistant
- Biocompatibility
- Some titanium alloys: shape memory effect, superelasticity

Applications
- Aircraft
- Spacecraft
- Chemical plant
- Artificial bone
- etc.

Table: Comparison between titanium and common metals

<table>
<thead>
<tr>
<th>Material</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>1665</td>
<td>660</td>
<td>1540</td>
</tr>
<tr>
<td>Price (¥/kg)</td>
<td>3,000</td>
<td>600</td>
<td>50</td>
</tr>
<tr>
<td>Production vol. (1/year-world)</td>
<td>50,000,000</td>
<td>800,000,000</td>
<td>1,100,000</td>
</tr>
<tr>
<td>Density</td>
<td>4.5</td>
<td>2.7</td>
<td>7.9</td>
</tr>
<tr>
<td>Price (¥/kg)</td>
<td>3,000</td>
<td>600</td>
<td>50</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>48</td>
<td>26.98</td>
<td>55.84</td>
</tr>
</tbody>
</table>

The Kroll process

Titanium production process

Ti ore + C + 2 Cl₂ → TiCl₄ (l) + CO₂

Features of the Kroll process:
- High-purity Ti can be obtained.
- Metal/salt separation is easy.
- Chlorine circulation is established.
- Efficient Mg electrolysis can be utilized.
- Reduction and electrolysis can be carried out independently.
- Process is complicated.
- Batch-type reduction process is used.
- Production speed is low.
- Chloride wastes cannot be utilized.

New Ti reduction process (EMR / MSE process)

Reduction:
- Titanium reduction
  - Cathode: TiO₂ + 4 e⁻ → Ti + 2 O₂⁻
  - Anode: CaCl₂
- Reductant production
  - Cathode: CaCl₂ + 2 e⁻ → Ca
  - Anode: C₂ + O₂ → CO₂ + 2 e⁻

Overall reaction
- TiO₂ + C → Ti + CO₂

Features of the EMR process:
- Resistant to iron and carbon contamination
- Semi-continuous process
- Reduction and electrolysis operations can be carried out independently
- Difficult metal/salt separation with oxide system
- Complicated cell structure

Chlorination

The reaction chamber

Carbon electrode
- Molten
- CaCl₂
- TiCl₄
- C
- Ca-Cl axis

Melted TiCl₄

Sponge titanium

Mg & TiCl₄ feed port

Fig. Schematic illustration of experimental apparatus in this experiment.

Graph: Thermodynamic analysis

Table: Analytical results of titanium ore (starting sample)

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<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ti</th>
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<tbody>
<tr>
<td>Mass %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>114</td>
<td>0.97</td>
</tr>
<tr>
<td>Ti</td>
<td>48.72</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Potentiostatic electrolysis

Voltage of 1.5 V was imposed.

Fig. Experimental result of potentiostatic electrolysis.

Table: Analytical results of titanium ore after electrolysis.

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<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass %</td>
<td>82%</td>
<td>18%</td>
</tr>
</tbody>
</table>

Future works

- A more efficient process for producing Ti-free Fe-Ti ore will be investigated.
- Behavior of chlorine in selective chlorination will be investigated.
- The process can also be applied to the new Ti production process.
- Material cost can be reduced by using low-grade ore.

This study (electrochemical method)

Thermodynamic analysis

Graph: Potential range for selective chlorination of TiO₂.

Table: Analytical results of titanium ore.

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<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
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<tbody>
<tr>
<td>Mass %</td>
<td>0.41</td>
<td>0.12</td>
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Selectivity of cathode reaction

Fig. Schematic illustration of experimental apparatus in this experiment.

Experiments

Table: Analytical results of titanium ore (starting sample).

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Experiment: Reduction and electrolysis operations can be carried out independently.

Potential lead (Ni wire), Stainless steel tube, Ar inlet, Rubber plug, Wheel flange, Reaction chamber, Thermocouple, Heater, Mild steel Crucible (Cathode), Nickel electrode, Carbon crucible (Anode), Ti ore, Molten salt (CaCl₂), Ceramic insulator

Chlorine recovery

Potential lead (Ni wire)

Potential lead (Ni wire)

Potential lead (Ni wire)

Fig. Schematic illustration of experimental apparatus in this experiment.

Experimental condition:

- T = 1100 K, t' = 9 h
- Atmosphere: Ar
- Voltage, E = 1.5 V

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Future works

- Selective chlorination of Ti ore by the electrochemical method was investigated, and 80 mass% Fe was successfully removed from low-grade Ti ore.