Introduction

Kroll Process

Chlorination:

TiO₂ + C + 2 Cl₂ → TiCl₄ + CO₂

Reduction:

TiCl₄ + 2 Mg → Ti + MgCl₂

Electrolysis:

MgCl₂ → Mg + Cl₂

Overall reaction:

TiO₂ + C → Ti + CO₂

At present, titanium is manufactured by the Kroll process. A new process technology is essential for titanium production.

Comparison between titanium and common metal.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.64</td>
<td>3.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu</td>
<td>0.27</td>
<td>0.16</td>
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Kroll process is huge exothermic reaction → It requires several days to produce titanium in large (ton) scale.

Electronically Mediated Reaction (EMR)

Conventional interpretation of metallothermic reaction

Feeding material → Reaction product

Metallothermic reaction

TiO₂ + 2 Ca → Ti + 2 CaO

Physical contact

Electrolysis

REDUCTION CHAMBER

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Ca</th>
</tr>
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<tbody>
<tr>
<td>Ti</td>
<td>3500</td>
<td>100</td>
</tr>
<tr>
<td>Ca</td>
<td>100</td>
<td>3500</td>
</tr>
</tbody>
</table>

Electronic contact

Metallothermic reaction

TiO₂ + TiCl₂ + Mg → Ti + 2 MgCl₂

Electrolysis

CaCl₂ → Ca + Cl₂

Overall reaction

TiO₂ + C + 2 Cl₂ → TiCl₄ + CO₂

Comparison with other studies

OS Process (Oono & Suzuki, 2002)

TiO₂ + 2 Ca → Ti + 2 CaO + Cl₂

Electrolysis

CaCl₂ + 2Cl → Cl₂ + Ca

Overall reaction

TiO₂ + C + 2 Cl₂ → TiCl₄ + CO₂

Simple process

Electrolysis

CaCl₂ + 2Cl → Cl₂ + Ca

Comparison with other studies

Low current efficiency

− Difficult metal/salt separation

− Sensitive to carbon and iron contamination

− High current efficiency

− Difficult metal/salt separation

− Sensitive to carbon and iron contamination

Experimental

In this study

Electrochemical reduction in the metallothermic reduction was utilized.

EMR/MSE process

This study

Current monitor

Fig. Schematic illustration of experimental apparatus for TiO₂ reduction using the EMR.

Table

Analytical results of the titanium powder obtained using an EMR at 1173 K

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<tbody>
<tr>
<td></td>
<td></td>
<td>t</td>
<td>η (%)</td>
</tr>
<tr>
<td>B1</td>
<td>99.6</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>B2</td>
<td>99.6</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>C1</td>
<td>99.9</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C2</td>
<td>99.9</td>
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<td>0.00</td>
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<tr>
<td>C3</td>
<td>99.9</td>
<td>0.00</td>
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</table>

Potential lead (Ti wire)

− Referencing lead (Ti wire)

− Ar inlet

− Wheel flange

− Stainless steel tube

− Thermocouple

− Reaction chamber

− Electric furnace

− Molten salt (CaCl₂)

− TiCl₄ powder

− Ca – Ni liquid alloy

− Sponge titanium

− Ceramic insulator

− Resistance to iron and carbon contamination

− Semi-continuous process

− Reduction and electrolysis operation can be carried out independently

− Difficult metal/salt separation

− Sensitive to carbon and iron contamination

− High current efficiency

− Semi-continuous process

− Reduction and electrolysis operation can be carried out independently

− Difficult metal/salt separation

− Sensitive to carbon and iron contamination

Discussion

3-D chemical potential diagram

Indicates that a redundant calcium need not to make physical contact with titanium oxides.

3-D chemical potential diagram

Fig. A three-dimensional chemical potential diagram for the system Ti-Ca-O at 1173 K.

(b) Depiction of the reaction pathway consistent with the chemical potential diagram.

Conclusion

EMR/MSE process (Oxide system)

− TiO₂ was reduced by metallothermic reaction through an electronically mediated reaction (EMR), and titanium powder was produced.

− Using EMR, titanium powder with 99.9% (metallic purity) containing 3500 ppm oxygen was obtained.

− EMR/MSE process is suitable for developing a (semi-)continuous and energy saving process.