Chemical Phenomena in Titanium Production

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Outline

• Background
• Routes to produce titanium
• Some basic physical properties
• Main process routes and key physical properties
• Conclusions
## South African’s Global Ti Position in 2006

<table>
<thead>
<tr>
<th></th>
<th>South Africa</th>
<th>World</th>
<th>Approximate Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>South Africa</td>
</tr>
<tr>
<td>Reserves</td>
<td>220 Mt TiO$_2$</td>
<td>1300 Mt TiO$_2$</td>
<td></td>
</tr>
<tr>
<td>Mineral Production</td>
<td>1090 kt TiO$_2$</td>
<td>5200 kt TiO$_2$</td>
<td>$175m p.a.</td>
</tr>
<tr>
<td>Slag Production</td>
<td>1090 kt TiO$_2$</td>
<td></td>
<td>$490m p.a.</td>
</tr>
<tr>
<td>Pigment Production</td>
<td>~20 kt TiO$_2$</td>
<td>5100 kt TiO$_2$</td>
<td>$37m p.a.</td>
</tr>
<tr>
<td>Sponge Production</td>
<td>Nil</td>
<td>125 kt p.a. Ti</td>
<td></td>
</tr>
<tr>
<td>Ingot Production</td>
<td>Nil</td>
<td>145 kt p.a. Ti</td>
<td></td>
</tr>
<tr>
<td>Mill Products</td>
<td>Nil</td>
<td>~90 kt p.a. Ti</td>
<td></td>
</tr>
</tbody>
</table>
## Approximate Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>Ti &amp; Alloys</th>
<th>Al &amp; Alloys</th>
<th>Fe &amp; Alloys</th>
<th>Ni &amp; Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strength (MPa)</strong></td>
<td>1300 max</td>
<td>500 max</td>
<td>1300 max</td>
<td>1400 max</td>
</tr>
<tr>
<td><strong>Density (kg/m³)</strong></td>
<td>4600</td>
<td>2700</td>
<td>7800</td>
<td>8400</td>
</tr>
<tr>
<td><strong>Normalized Strength/weight</strong></td>
<td>1</td>
<td>0.85</td>
<td>0.65</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Elasticity (GPa)</strong></td>
<td>115</td>
<td>72</td>
<td>215</td>
<td>200</td>
</tr>
<tr>
<td><strong>M.P. (°C)</strong></td>
<td>1668</td>
<td>660</td>
<td>1538</td>
<td>1455</td>
</tr>
<tr>
<td><strong>Rel. Corrosion Resistance</strong></td>
<td>Very high</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td><strong>Carbon Compatibility</strong></td>
<td>Resistant</td>
<td>Corrosion</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bio Compatibility</strong></td>
<td>Excellent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>T Exp. Coeff. (10⁻⁶/°C)</strong></td>
<td>±8.5</td>
<td>±20</td>
<td>±12</td>
<td>±11</td>
</tr>
<tr>
<td><strong>Conductivity (W/m°C)</strong></td>
<td>7</td>
<td>180</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td><strong>Color</strong></td>
<td>Aesthetic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Kyushu National Museum
Photo courtesy of the Kyushu National Museum

The Race

New Primary Metal Technology:

- Europe - Ginatta
- Japan
  - Ono & Suzuki
  - JTS
- USA
  - Armstrong
  - ADMA
- UK – FFC Process
- Australia – TiRO Process
- South Africa
  - Peruke
  - CSIR

CHINA – Rapid expansion using known technology, cheap labor and large domestic market
Melting & boiling points of some metals and salts ($\text{Ti}_{\text{M.P.}} = 1668^\circ\text{C}$)

<table>
<thead>
<tr>
<th>Element</th>
<th>Metal</th>
<th>Chloride</th>
<th>Fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>660</td>
<td>193</td>
<td>1291 subl.</td>
</tr>
<tr>
<td>Li</td>
<td>181</td>
<td>610</td>
<td>848</td>
</tr>
<tr>
<td>Na</td>
<td>98</td>
<td>801</td>
<td>996</td>
</tr>
<tr>
<td>Mg</td>
<td>650</td>
<td>714</td>
<td>1263</td>
</tr>
<tr>
<td>Ca</td>
<td>842</td>
<td>775</td>
<td>1418</td>
</tr>
<tr>
<td>Al</td>
<td>2519</td>
<td>447</td>
<td>1291 subl.</td>
</tr>
<tr>
<td>Li</td>
<td>1342</td>
<td>1383</td>
<td>1673</td>
</tr>
<tr>
<td>Na</td>
<td>883</td>
<td>1465</td>
<td>1704</td>
</tr>
<tr>
<td>Mg</td>
<td>1088</td>
<td>1412</td>
<td>2227</td>
</tr>
<tr>
<td>Ca</td>
<td>1484</td>
<td>2209</td>
<td>2534</td>
</tr>
</tbody>
</table>
Salt Vapour Pressures

![Graph showing vapour pressures of various salts against temperature](image-url)
Hunter & Kroll processes

Hunter: Substoichiometric
Kroll: Excess Mg

Hunter: Aqueous leach
Kroll: Vacuum distillation

TiCl₄ Na/Mg

Reaction

Molten salt

Separation

Mg/Na and salt

Ti Sponge
Ginatta Process

Temperature > 1670°C

Electrolyte
- Chlorides: Only Ca & Ba
- Fluorides: Mg, Ca, Sr, Y
  Density of Ba, La & Ce too high

Lining
- Oxides: Only Y & Sc
- Freeze lining
FFC and Ono & Suzuki Processes

Low oxygen potential of metal of the salt cation

\[ \frac{1}{2}RT \ln P \]

Temperature (K)
JTS Process

High solubility of Ca in CaCl$_2$

B.P. of CaCl$_2$ > M.P. of Ti

$\rho_{\text{CaCl}_2} < \rho_{\text{Ti}}$
Armstrong Process

Advantage of low M.P. of Na

Na → TiCl₄ → Reaction → Excess Na → Na, Solid NaCl & Ti Powder → Na → Separation → NaCl and Ti Powder → H₂O → NaCl/Ti Separation → Aqueous NaCl → Ti Powder
TiRO Process

\[ Ti + MgCl_2 \rightarrow TiCl_4 \]

\[ MgCl_2 \rightarrow \text{Effluent, } H_2 \text{ formation, re-crystallization of anhydrous } MgCl_2 \]

\[ MgCl_2 \cdot H_2O \leftrightarrow MgO + 2HCl \]

Evaporation

Large mass/energy
Continuous operation under vacuum

\[ T_{\text{M.P.Mg}} < T_{\text{reactor}} < T_{\text{M.P.MgCl2}} \]
Peruke Process

M.P. of Al determines $T_{\text{Reactor}}$

Low solubility of $\text{AlF}_3$ in water $\approx 5.6\text{g/lit}$

$\text{AlF}_3$ does not melt: Physical separation does not work well

Separation by sublimation

Large mass/energy

Continuous operation under vacuum (low vapour pressure)
Continuous metallothermic reduction in molten salt (CSIR)

M.P. of salt determines reactor temperature, construction materials & heat exchanger design.

M.P. of salt and metal affects electrolyser temperature.

Oxide/chloride equilibrium of salt determines salt recovery process.
Product Removal
Product Morphology
Conclusions

• The obvious: Basic physical properties of the relevant chemicals have major effects on the selection of the chemical route to produce titanium and on the associated process and equipment designs.

• However, there is no consensus as to what process would be better than the Kroll process and many different approaches are being pursued by different organisations around the world.
THANK YOU

The support of the DST is sincerely appreciated