Ongoing development of the TiRO™ process

Continuous direct titanium powder production

Christian Doblin, Ongoing development of the TiRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
CSIRO Titanium Technologies - from ore to more

- We pull resources from the overall pool of 6,500 dedicated employees of CSIRO.
- The Titanium Technologies group taps into the skills of 70 CSIRO scientists and engineers.
- We strive to build a titanium industry that is more efficient and affordable.

Titanium Technologies

Metal Production
- TIRO
- Alloys Process
- Novel Alloys

Powder to Product
- Sheet
- Wire
- Extrusions
- Billet
- Powder Prep

Manufacturing
- Cold Spray
- Australian Additive Manufacturing Init.
- Machining Technologies

Victorian Direct Manufacturing Centre
TiRO™ Process

\[ \text{TiCl}_4 + 2\text{Mg(l)} \rightarrow \text{Ti(s)} + 2\text{MgCl}_2 \]

Christian Doblin, Ongoing development of the TiRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
Christian Doblin, Ongoing development of the TIRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
TiRO™ intermediate product (from FBR)

- The FBR product is near spherical particles ($d_{50} \approx 300 \mu m$) comprising a continuous MgCl$_2$ matrix with much smaller uniformly dispersed Ti particles
- Evidence of agglomeration occurring

![Photograph of intermediate “poppy seeds”](image1)
![ESEM micrograph of “poppy seeds”](image2)

**Particle size distributions of FBR product**

Christian Doblin, Ongoing development of the TIRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
TiRO™ intermediate product (poppy seed)

- Small titanium particles dispersed throughout a MgCl₂ substrate \((d_{50} = 1.7 \, \mu m)\)
- Some voidage and unreacted Mg in cores

ESEM micrograph of “poppy seed”

Micro CT scan particle voidage (dark areas) unreacted Mg (bright spot) at the cross-hairs

Christian Doblin, Ongoing development of the TIRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
TiRO™ poppy seed chemical composition

- Nominally 20 wt% Ti, 80 wt% MgCl₂ (Based on reaction stoichiometry)
- O < 0.03 wt% target (enables production of CP2 titanium product)
  - Potential to produce CP1 titanium
- N < 0.01 wt%
- Minor elements in the ppm range
  - No evidence of contamination from vessel wall
  - Fe <100 ppm; Ni ~50 ppm; Cr ~30 ppm
- Some unreacted Mg metal present (average ~0.5 wt%)
TiRO™ Continuous Vacuum Distillation Unit (CVDU-X)

Christian Doblin, Ongoing development of the TIRO™ process
October 7-10, 2012 • Atlanta, Georgia, USA
Continuous vacuum distillation of “poppy seed”

- Serves two purposes
  - Separates MgCl₂ from Ti
  - Sinters Ti to reduce specific surface area & hence limit formation of surface oxide layer and limit O content to <0.2 wt%
- Convey “poppy seed” on a S/Steel conveyor belt
- Operating temperature 700°C to 950°C
- Maintain pressure below MgCl₂ triple point
  - 0.13 mbar
- Residence time 60 to 180 min
- Feed up to 1 kg/h “poppy seed” (200 g/h Ti)
- Ti “biscuit” peels from belt
TiRO™ vacuum distilled titanium biscuit

- Lightly sintered
- Limited mechanical strength, Very friable
- Residual Cl = f(process conditions)
  - Routinely achieve < 300ppm Cl
  - Lowest is 100 ppm (limitation of current analytical technique)
- O content = f(feed, process conditions)
  - Routinely achieve < 0.25 wt% O
  - Lowest is 0.15 wt% O
- Feed and product handling can be improved further

- Cl in product reduced by washing
- O reduced by increased sintering

Christian Doblin, Ongoing development of the TIRO™ process
October 7-10, 2012 • Atlanta, Georgia, USA
TiRO™ vacuum distilled titanium product

- Low density partially hollow spheres
- Free flowing powder when broken up/ground

<table>
<thead>
<tr>
<th>TiRO™ “Biscuit” treatment</th>
<th>d_{10} [µm]</th>
<th>d_{50} [µm]</th>
<th>d_{90} [µm]</th>
<th>Bulk density, [kg/m³]</th>
<th>Tap density, [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mortar and pestle</td>
<td>=250</td>
<td></td>
<td></td>
<td>1.45</td>
<td>1.73</td>
</tr>
<tr>
<td>Ring milled for 2 min</td>
<td>106</td>
<td>211</td>
<td>348</td>
<td>2.23</td>
<td>2.59</td>
</tr>
<tr>
<td>Ring milled for 5 min</td>
<td>735</td>
<td>177</td>
<td>311</td>
<td>2.05</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Christian Doblin, Ongoing development of the TiRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
Techno-economics of TiRO™

Source: Annual Reports, various

• Greenfield Comparison:
  – Median Kroll Plant Capital Cost US$ 35k/tpa
  – TiRO™ ‘Worst Case’ Capital Cost US$ 15k/tpa

• Expansion Comparison:
  – Average Kroll Plant Capital Cost US$ 19k/tpa
  – TiRO™ ‘Worst Case’ Capital Cost US$ 12k/tpa

TiRO™ capital cost is significantly below Kroll plants
### Operating Cost - comparison

Assuming common cost for TiCl₄ and Mg

<table>
<thead>
<tr>
<th>Company</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>Average</th>
<th>TiRO™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sundry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance</td>
<td>$0.00</td>
<td>$1.00</td>
<td>$2.00</td>
<td>$3.00</td>
<td>$4.00</td>
<td>$5.00</td>
<td>$6.00</td>
<td>$7.00</td>
<td>$8.00</td>
</tr>
<tr>
<td>Labour</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity &amp; utilities</td>
<td>$0.00</td>
<td>$1.00</td>
<td>$2.00</td>
<td>$3.00</td>
<td>$4.00</td>
<td>$5.00</td>
<td>$6.00</td>
<td>$7.00</td>
<td>$8.00</td>
</tr>
</tbody>
</table>

Source: Ti-Metal, TZMI

*Costs adjusted for inflation from 2006

---

**Potential for TiRO™ product to be used as a sponge replacement while the CP grade powder market is grown**

---

Christian Doblin, Ongoing development of the TIRO™ process

October 7-10, 2012 • Atlanta, Georgia, USA
TiRO™ - the next year

• Scale-up CVDU from 0.2 to 2.5 kg/h Ti
• Design an integrated 2.5 kg/h TiRO™ process
• Construct and operate an integrated 2.5 kg/h TiRO™ process at commercial partner’s site in Laverton, Victoria (Coogee Chemicals)
  – 1000 m² facility
• Produce powder for internal & third party evaluation

Example of Ti sheet made with TiRO™ powder
Thank-you

Team TiRO™
• Christian Doblin
• David Freeman
• Matt Richards
• Andrew Brent
• David McCallum
• Daniella Caruso

Techno-economic evaluation
• Alex Kingsbury

Dr Christian Doblin
CSIRO Future Manufacturing Flagship
Project Leader – Titanium metal production

+61 3 9545 8658
christian.doblin@csiro.au
http://www.csiro.au/TitaniumTechnologies

Christian Doblin, Ongoing development of the TIRO™ process
October 7-10, 2012 • Atlanta, Georgia, USA