Low Cost Titanium Powder Processes to Facilitate Near Net Shape Manufacture

Grant Wellwood
Who are CSIRO?

- CSIRO is Australia's national science agency & one of the largest in the world.
  - 2005-6 revenue >US$700 million (US$450 million appropriation)

- > 80 years of activity in research

- Over 6,500 staff across 57 sites
  - >60% degree qualified,
  - >2,000 PhD’s,
  - >470 Masters

- National Research Flagships-focus science on national priorities
  - Light Metals Flagship
    - Magnesium, aluminum, titanium (≈US$6Million/annum)
Australia

- 80,760 ktTi$_{eq}$
  - (15%W)
  - 114 years

- 707 ktTi$_{eq}$
  - (25%W)

- 580 ktTi$_{eq}$

- 127 ktTi$_{eq}$
  - (18% Aust mine output)

- 121 ktTi$_{eq}$
  - (4.8%W)

Ref: Geoscience Australia
“Australia’s Identified Mineral Resources 2005”
• Market limited by cost
• Cost high due to processing difficulties, containment, contamination
• LMF differentiated by:
  - Continuous, low temperature processes
  - Net shape manufacturing

CSIRO’s Strategy

- **Enabling factor** = Low cost Ti, i.e. primary research focus,

- Continuous production of powder metallurgy (PM) compatible Ti powder → Savings,

- Review Ti production pathways
  - Fluidised bed (FB) reduction approach identified for CP grade powder,
    - TiRO™ project established to develop FB approach
  - Novel chemistry based approach identified for Ti alloy powder,
    - TiAlloysDirect™

- Other Flagship-sponsored teams working on upstream & downstream aspects of the integrated process

- 2006/7 Investment in Ti US$6 Million
Demonstrate the production of Ti metal powder by the deposition of Ti produced from the reaction of TiCl$_4$ and Mg in a gas-solid contacting reactor.

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

\[
\begin{align*}
\text{TiCl}_4 + \text{Mg} & \rightarrow \text{TiCl}_2 + \text{MgCl}_2 \\
\text{TiCl}_2 + \text{Mg} & \rightarrow \text{Ti} + \text{MgCl}_2
\end{align*}
\]

Ref: Nagesh et al., 2004

Fig. 7—(a) through (c) Proposed reaction mechanism for sponge formation in Kroll reactor.

Ref: Nagesh et al., 2004
Temperature Operating Window

Magnesium-Titanium Tetrachloride Reaction System

- **Temperature (℃)**: Ranges from 0 to 2,000
- **Phase States**:
  - **Gas** (turquoise)
  - **Liquid** (blue)
  - **Solid** (yellow)

Materials:
- **TiCl₄**
- **Mg**
- **MgCl₂**
- **Ti**

The diagram illustrates the phase behavior of the magnesium-titanium tetrachloride reaction system at different temperatures.
TiCl₂ + MgCL₂
TiRO Process

Mg

TiCl₄

Process Intermediate
(MgCl₂/Ti composite)

Ar

MgCl₂

Ti Powder
TiRO™ Reactor Module

- Basis of Design: 250 g Ti metal/h
  - 980 g TiCl₄/h
  - 250 g Mg/h
  - 980 g MgCl₂/h
  - Ar 13-16 kg/h
ESEM of Ti/MgCl$_2$ Composite
## TiRO Quality Comparison

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Percent Dry Basis</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>General Purpose grade</td>
<td>Magnesium Reduced then leached</td>
<td>Magnesium Reduced then Vacuum Distilled</td>
<td>Grade 1</td>
<td>Grade 2</td>
<td>Grade 3</td>
<td>Grade 4</td>
<td>Grade 5</td>
<td>Grade 7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.020</td>
<td>0.015</td>
<td>0.015</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.08</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.05</td>
<td>0.5</td>
<td>0.08</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.05</td>
<td>0.05</td>
<td>0</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.2</td>
<td>0.2</td>
<td>0.12</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Iron</td>
<td>0.15</td>
<td>0.15</td>
<td>0.12</td>
<td>0.18</td>
<td>0.25</td>
<td>0.35</td>
<td>0.4</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>Water</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.15</td>
<td>0.1</td>
<td>0.1</td>
<td>0.18</td>
<td>0.25</td>
<td>0.35</td>
<td>0.4</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>Chromium</td>
<td>0</td>
<td>0</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
- Robust process
- High single pass conversion of TiCl₄ (i.e. high rate)
- No stoichiometric excesses required
  (i.e. No reagent recovery step needed)
- High yield
  - Minimum losses to reactions with retort Fe
- Counter-intuitive process, intellectual property and
  know-how generated
Ti Alloy Process

Stage 1

Stage 2

By-Product Processing

Product Recovery

Meter Reagent 1

Meter Reagent 2

Meter Reagent 3

Product Recovery

By-Product Processing
Direct production of “designer” alloys

A wide range of alloys can be produced
LMF Powder Cost Projections
Creating a Titanium Industry in Australia