Transformational Non-Kroll Process
Hydrogenated Titanium Powder Production

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Powder Metallurgy (PM) Powder metallurgy (P/M) is an attractive method to reduce cost of titanium components while improving their chemical and physical properties.

Solid-State Powder Metallurgy is a mature industry for other metals, such as stainless steels, copper, brass and aluminum alloys.

* PM part manufacturing was US$2.1 billion in 2011 versus only US$5 million for titanium

* Metal Powder Report, 03 October, 2012

Titanium powder metallurgy is not developed.
Issues that have hindered titanium powder metallurgy industry development

P/M Ti alloys did not meet the requirements of ASTM and AMS standards

1. Chemistry issues:
   • High impurities content – the need to remove Chlorine, Magnesium, Sodium (only melting can remove impurities)
   • High oxygen content (related to high surface area of titanium powders) – 0.20% O max per AMS 4928L

2. Properties issues:
   • Inferior low cycle fatigue and fatigue related properties, inferior fracture toughness
   • “Weld-ability” Issues
One of the reasons why titanium PM industry is not developed is lack of low cost and good quality titanium powder.

- **ADMA Low Cost Innovative Ti Powder Production Technology**
  (U.S. Patent 6,638,336 B1)

- **ADMA Blended Elemental Powder Metallurgy Approach**
  (US Patent 7,993,577 B2)
Extensive review of the various routes of titanium powder production indicates that a magnesium reduction followed by hydrogenation may be the most cost effective approach to produce the high quality titanium powder.

The powder production technology developed by ADMA Products, Inc. is based on breaking up the titanium sponge mass upon its saturation with hydrogen (or conversion into extremely brittle titanium hydride TiH₂) which breaks up the sponge mass into titanium hydride powder.
Titanium Hydride Powder Production

Modified Kroll Process
(U.S. Patent No. 6,638,336 B1)

Hydrogenated titanium powders are produced in two basic stages:
- titanium tetrachloride reduction with magnesium;
- titanium sponge purification by vacuum distillation and hydrogenation;

Use of hydrogen considerably reduces vacuum distillation time, increases furnace output, reduces electric power consumption, labor and production costs.

Dr. Duz, R&D Director, ADMA Products
October 7-10, 2012 • Atlanta, Georgia, USA
ADMA Titanium Hydride Powder Production

ADMA received $1.4M Congressional award under the 2009 Defense Appropriations Act to begin production of hydrogenated titanium powder in the USA.

Lab-scale unit for hydrogenated Ti powder production at ADMA Products, Inc.

TiH$_2$ sponge
### Typical Chemical Analysis of ADMA TiH$_2$ powder

<table>
<thead>
<tr>
<th>Material</th>
<th>Fraction of total mass of specified impurities, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>ADMA TiH$_2$ powder</td>
<td>0.03 – 0.16</td>
</tr>
<tr>
<td>ASTM B348 Grade 2</td>
<td>0.300</td>
</tr>
</tbody>
</table>

* Average from over 20 production runs
The additional titanium hydride powder introduced together with titanium tetrachloride beneficially affects the kinetics of the magnesium reduction process due to the formation of additionally-emitted atomic hydrogen, which helps to reduce oxides in the system, cleans the inter-particle interfaces of the product, and enhances the diffusion between components of powder mixture.
Advantages of ADMA TiH₂ Powder Production Process Over Conventional Technology

- Use of hydrogen considerably reduces vacuum distillation time.
- Use of hydrogen completely eliminates the comminution process (boring, shearing, crushing).
- Use of hydrogen reduces reduction time and increases Mg utilization.

Cost of ADMA TiH₂ powder is 15% lower than cost of conventional Ti sponge.
ADMA Blended Elemental Powder Metallurgy Approach
(US Patent 7,993,577 B2)

Eventually the hydrogen is completely removed from material during sintering

Hydrogenation followed by simultaneous de-hydrogenation & sintering are two innovative aspects of our invented process that are the key in reducing the cycle time to <24 hours (i.e., 5-fold reduction) leading to ~50% energy savings and cost reduction of ~20%.
Weapon Components Developments
CIP/Sinter/Rotary Forging

Ti-6Al-4V round bar stock for manufacturing the weapon components using the TiH$_2$ powder produced at the ADMA laboratory scale unit.

Ti-6Al-4V billet manufactured from ADMA TiH$_2$ powder by Cold Isostatic Pressing and Sintering

0.875” Dia x 12ft long Ti-6Al-4V round bars
# Weapon Components Developments

## Chemical Analysis of P/M Ti-6Al-4V CIP/Sinter/Rotary Forged Bars Produced from ADMA TiH₂ Powder

<table>
<thead>
<tr>
<th>Ti-6Al-4V</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>H</th>
<th>Ti</th>
<th>Other, Each</th>
<th>Other Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADMA TiH₂ Powder</td>
<td>5.83</td>
<td>3.72</td>
<td>0.29</td>
<td>0.017</td>
<td>0.029</td>
<td>0.189</td>
<td>0.012</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>ASTM B348</td>
<td>5.5-6.75</td>
<td>3.5-4.5</td>
<td>0.40</td>
<td>0.08</td>
<td>0.05</td>
<td>0.200</td>
<td>0.015</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>AMS 4928R</td>
<td>5.5-6.75</td>
<td>3.5-4.5</td>
<td>0.30</td>
<td>0.08</td>
<td>0.05</td>
<td>0.200</td>
<td>0.0125</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
</tr>
</tbody>
</table>
Dr. Duz, R&D Director, ADMA Products

October 7-10, 2012 • Atlanta, Georgia, USA

Weapon Components Developments

**Room Temperature Tensile Properties**

<table>
<thead>
<tr>
<th></th>
<th>UTS, ksi</th>
<th>YS, ksi</th>
<th>Elongation, %</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADMA TiH₂ Powder</td>
<td>154 – 155</td>
<td>141 – 142</td>
<td>15.8 – 16.5</td>
<td>38 - 40</td>
</tr>
<tr>
<td>Na Reduced Ti Powder</td>
<td>139</td>
<td>125 – 126</td>
<td>9.0 – 10.0</td>
<td>19 - 20</td>
</tr>
<tr>
<td>AMS 4928R</td>
<td>135 Min.</td>
<td>125 Min.</td>
<td>10 Min.</td>
<td></td>
</tr>
</tbody>
</table>

**Microstructure of P/M Ti-6Al-4V bars**

- **ADMA TiH₂**
- Sodium Reduced Ti

Primary alpha (light etching) in a transformed beta matrix containing acicular alpha (dark etching)
Pilot Scale Unit for Manufacturing of Hydrogenated Titanium Powder (660 lbs/cycle)

ADMA received a Defense Appropriations Act Congressional award of $1.2 M to increase production of Hydrogenated Titanium Powder

Pilot scale unit for hydrogenated titanium powder (TiH$_2$) production (660 lbs/run) is being manufactured
CONCLUSIONS

1. Innovative low cost magnesium reduction process for manufacturing the hydrogenated titanium powder (TiH$_2$) was developed

2. Laboratory scale unit (10 lbs/run) for TiH$_2$ powder production was built and installed at ADMA facility (Hudson, Ohio)


4. Pilot scale unit with a capacity of 660 lbs/run for TiH$_2$ powder production is being build and will be installed at ADMA facility by the end of the year 2012
Thank You for Your Attention