Manufacturing of Hydrogenated Titanium Powders and Titanium Components for Critical Applications

Vladimir Duz, Vladimir Moxson, Mykhailo Matviychuk, Andrey Klevtsov

ADMA Products Inc., 1890 Georgetown Road, Hudson Ohio 44236, USA
Presentation overview

• ADMA innovative process for manufacturing of Titanium hydride (TiH$_2$) powder

• Advantages of ADMA Process compare to conventional processes

• Manufacturing of Titanium Components for Critical Applications from Hydrogenated Titanium Powder
Why Does Titanium Presently Cost So Much?

**High extracting costs**
- strong bonding between titanium and oxygen;
- requirements to get relatively low levels of other elements;

**High processing costs**
- high temperature processing requires conditioning (surface areas contaminated at the processing temperatures, alpha case and surface cracks must be removed after each thermo-mechanical processing step);

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Powder Metallurgy (PM) Powder metallurgy (P/M) is an attractive method to reduce the cost of titanium components (low buy-to-use ratio: scrap rate ≤ 2%) 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$2.2 billion in 2014* versus only $5 million U.S. for titanium).

* Metal Powder Report, 2014
Issues that have hindered titanium powder metallurgy industry development

1. High cost of raw materials
   - Ti sponge fines generated in Ti sponge production (low yield, high impurities content);
   - HDH powder (high cost, high oxygen content)

2. 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
**Conventional Technology (Kroll Process)**

*Kroll’s Process:* \(\text{TiCl}_4 \text{ (gas)} + 2\text{Mg (liquid)} \rightarrow \text{Ti (sponge, solid)} + 2\text{MgCl}_2 \text{ (liquid)}\)

The key challenge of Kroll’s process is to remove \(\text{MgCl}_2\) entrained in the Ti sponge by vacuum distillation.

The sponge is very strong and cannot be easily crushed to “release” the entrained \(\text{MgCl}_2\) and aid in its removal.

The main drawback of Kroll’s process is that the cycle time, i.e. purification of Ti sponge by vacuum distillation can exceed 4-5 days.
Extensive review of various routes of titanium powder production indicates that magnesium-hydrogen 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 is based on breaking up the ductile titanium sponge mass upon its saturation with hydrogen, and converting it into extremely brittle titanium hydride powder (TiH$_2$).
ADMA Process for Hydrogenated Titanium Powder Production

ADMA’s proposed process can transform the Ti production because it overcomes the technical challenges of the Kroll’s process by partially replacing molten Mg with H₂ gas as a reducing agent to produce TiH₂ instead of Ti.

TiCl₄ (gas) + (1-2)H₂ (gas) + (1-2)Mg (liquid) = TiH₂ (sponge, solid) + (1-2)MgCl₂ (liquid) + (0-2)HCl (gas)
Advantages of ADMA TiH₂ Powder Production Process Over Conventional Technology

- Use of hydrogen reduces reduction time and increases Mg utilization
- Use of hydrogen can shorten the time for removal of MgCl₂ by vacuum distillation process by 80%
- Use of hydrogen completely eliminates the comminution process (cutting, boring, shearing, crushing) of Ti sponge block
- TiH₂ sponge mass can be ground to powder in same retort, transported and packed under argon or vacuum

Cost of ADMA TiH₂ powder is considerably lower than cost of conventional Ti sponge
Grinding of brittle TiH₂ sponge directly in the retort

The brittle titanium hydride (TiH₂) sponge can be crushed inside the retort, and fine TiH₂ powder transferred and packed under argon without any contact with air.
Advantages of ADMA Titanium Hydride Powder

✓ Lower cost
✓ Lower flammability
✓ Higher resistance to oxidation
✓ Lower impurity content (Cl, O, Mg, C) in sintered products
Pilot scale unit for manufacturing of TiH₂ powder (annual capacity 250,000 lbs)

Typical O₂ content from run to run

Typical H₂ content from run to run

<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 TiH₂ powder</td>
<td>0.03 – 0.16</td>
</tr>
<tr>
<td>ASTM B348 Grade 2</td>
<td>0.300</td>
</tr>
</tbody>
</table>

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ADMA Blended Elemental Powder Metallurgy Approach  
(US Patent 7,993,577 B2)

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%.
High Density (98-99%) Blended Elemental P/M Titanium Alloy Parts

Employment of TiH₂ instead of Ti powder allows attainment of 99+% density and mechanical properties equivalent to those of ingot materials with most cost-effective room temperature compaction and sinter approach (without additional hot temperature post-processing).

Hydrogen is completely removed from material during sintering.
Influence of Compaction Pressure

**TiH$_2$ – based compacts:**
- Fine crushed hydride fragments;
- Fine pores independently on pressure applied

Pores are easy to heal upon sintering $\rightarrow$ high sintered density

**Ti – based compacts:**
- Deformed ductile particles;
- Relatively coarse pores (size depends on pressure applied);

Pores partially survived upon sintering

**Density:**
- To attain sufficient sintered density compaction pressure value is not critical parameter for titanium hydride powder contrary to titanium powder.
- Sintered densities of TiH$_2$ blends higher than in equivalent Ti-based blends

This unique feature of the titanium hydride approach is attributed to compaction mechanism of low strength and brittle hydride particles.
Atomic hydrogen decreases the impurities content in P/M Titanium products to the level of AMS specifications
Impurities on TiH$_2$ Powder Surface (photo-electron spectroscopy)
Mass Spectroscopy of Gases Emitted (450°C)

Emission of gases in the temperature range of hydrogen emission resulting from the reaction of atomic hydrogen with impurities

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Dehydrogenation: Cleaning Action (O)

Mass-spectrometry results

Temperature, °C

Intensity of H₂ emission

Intensity of H₂O emission

H₂O(TiH₂)    H₂O(Ti)

0  100  200  300  400  500  1000  1500  2000  2500  3000  3500  4000

Hydrogenated powder  0.16
Green compact Ti-6Al-4V  0.22
Ti-6Al-4V alloy after sintering  0.12

Reduction of TiO₂ surface scales upon dehydrogenation:

TiO₂ → TiO → Ti
Dehydrogenation: Cleaning Action (Cl)

\[ \text{MgCl}_2 + 2H = Mg + 2HCl \]

HCl emission indicates on cleaning of particle surface from chlorine by hydrogen.
Processing Steps for the B/E Titanium Alloy Parts Production

ADMA Titanium P/M “in house” Processes

- TiH₂ Powder
- Die Press
- Direct Powder Rolling
- Cold Isostatic Pressing
- Vacuum Sintering
- Finished Products

Post-Processing Outside vendors

- Forging
- Hot Rolling (Flat & Round)
- Extrusion
- Flowform
- Ring Rolling

Ti alloy compositions
- CP Ti
- Ti-6Al-4V
- Ti-3Al-2.5V
- Ti-6-6-2
- Ti-6-2-4-2
- Ti-1Al-8V-5Fe
- Metal Matrix Composites
- TiAl
- Other Ti alloys

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Die-Press + Sinter

Die-pressing is cost effective in producing simple or complex parts at, or very close to, final dimensions in production rates which can range from a few hundred to several thousand parts per hour.

As a result, only minor, if any, machining is required. P/M parts also may be sized for closer dimensional control and/or coined for both higher density and strength.
Titanium and Titanium Alloys Aircraft Components

Die-press/Sinter

<table>
<thead>
<tr>
<th>Material</th>
<th>YS, ksi</th>
<th>UTS, ksi</th>
<th>El. %</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V (Die-press/Sinter)</td>
<td>121 - 123</td>
<td>140 - 142</td>
<td>13 - 15</td>
<td>28</td>
</tr>
<tr>
<td>Ti-6Al-4V, AMS 4928</td>
<td>120</td>
<td>130</td>
<td>10</td>
<td>25</td>
</tr>
</tbody>
</table>

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Direct Powder Rolling + Sinter

- Powder Rolling Mill
- Saw Cut
- Ti Alloy Plate
- Vacuum Furnace
- Compacted Strip
- Molybdenum Plate
- Re-Rolling Mill
Direct Powder Rolling of Ti Alloy Foil, Sheet, and Plate at ADMA

0.005” – 0.250” thick x up to 25” wide
Porous Titanium, Zirconium, Niobium, and Stainless Steel Plates

- Life support systems for NAVY, Air force, NASA
- Stand-alone hydrogen generators
- Energy storage Smart Grid Storage™
Cold Isostatic Pressing + Sinter
Cold Isostatic Pressing + Sintering

- Cold Isostatic Pressing
- Sintering
  - Post-processing
    - Forging
    - Flowform
    - Ring Rolling
    - Extrusion

- Rolling
  - Flat (foil, sheet, plate)
  - Round (bar, rod)
Cold Isostatic Pressing

Sintering

Forging

“... material met the forging spec requirements, as well as the plate spec requirements (MIL-DTL-46077) ... this is the best result we have seen from any PM based, no melt, low cost material.” (BAE 7-6-2010)

<table>
<thead>
<tr>
<th></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>CIP/Sinter</td>
<td>6.16</td>
<td>4.21</td>
<td>0.080</td>
<td>0.009</td>
<td>0.021</td>
<td>0.179</td>
<td>0.0018</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>ASTM/AMS</td>
<td>5.5 – 6.75</td>
<td>3.5-4.5</td>
<td>0.30</td>
<td>0.080</td>
<td>0.050</td>
<td>0.20</td>
<td>0.0125</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
</tr>
</tbody>
</table>

Room Temperature Tensile Properties

<table>
<thead>
<tr>
<th>P/M Ti-6Al-4V</th>
<th>Ultimate Tensile Strength, ksi</th>
<th>Yield Strength, ksi</th>
<th>Elongation, %</th>
<th>Reduction of Area, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.375” thick</td>
<td>144 – 149</td>
<td>132 – 136</td>
<td>14.0 – 15.5</td>
<td>34 – 38</td>
</tr>
<tr>
<td>ASTM</td>
<td>130</td>
<td>120</td>
<td>10</td>
<td>25</td>
</tr>
</tbody>
</table>
Ti-6Al-4V - CIP/Sinter/Hot Rolling

| Cold Isostatic Pressing | Sintering | Hot Rolling |

Ti-6Al-4V - CIP/Sinter/Hot Rolling

<table>
<thead>
<tr>
<th>Room Temperature Tensile Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/M Ti-6Al-4V</td>
</tr>
<tr>
<td>0.75” thick</td>
</tr>
<tr>
<td>0.50” thick</td>
</tr>
<tr>
<td>ASTM</td>
</tr>
</tbody>
</table>

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The blended elemental RTI and TIMET hot-rolled P/M Ti-6Al-4V alloy mill products met the AMS Specification mechanical property requirements for both static loading, as well as damage tolerant fracture toughness and cyclic S/N fatigue endurance limit for aerospace applications.

The powder-based Ti-6Al-4V rolled mill products show static tensile, fatigue S/N, and fracture properties matching similarly-processed ingot-based hot-rolled products
Extrusion Process for BE P/M Ti-6AL-4V Alloy

Extrusions up to 36-foot long were fabricated and analyzed at front, mid-length, and back and found to be uniform with respect to oxygen content & microstructure.

<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>CIP/Sinter</td>
<td>6.2-6.4</td>
<td>4.04-4.30</td>
<td>0.15</td>
<td>0.01</td>
<td>0.01</td>
<td>0.20</td>
<td>0.0125</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>0.20</td>
<td>0.0150</td>
<td>Bal</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ti-6Al-4V</th>
<th>UTS (ksi)</th>
<th>0.2% YS (ksi)</th>
<th>% El.</th>
<th>% RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADMA P/M</td>
<td>156 – 157</td>
<td>134 – 135</td>
<td>12 - 13</td>
<td>28</td>
</tr>
<tr>
<td>Ingot Based</td>
<td>140 - 142</td>
<td>125 – 127</td>
<td>12</td>
<td>27</td>
</tr>
</tbody>
</table>
Powder Metallurgy Ti alloy Round Bars

**Ti-6Al-4V FRED SERT (IBIF)**

- Cold Isostatic Pressing
- Sintering
- Extrusion
- Rolling
- Rotary Forging

### Ti-6Al-4V Al V Fe C N O H Ti Other, Each Other, Total

<table>
<thead>
<tr>
<th></th>
<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 P/M</td>
<td>6.16</td>
<td>4.32</td>
<td>0.08</td>
<td>0.018</td>
<td>0.029</td>
<td>0.19</td>
<td>0.0060</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
<td></td>
</tr>
<tr>
<td>Ingot based</td>
<td>6.34</td>
<td>4.05</td>
<td>0.16</td>
<td>0.020</td>
<td>0.007</td>
<td>0.20</td>
<td>0.0070</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
<td></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>0.20</td>
<td>0.0150</td>
<td>Bal.</td>
<td>&lt;0.10</td>
<td>&lt;0.40</td>
<td></td>
</tr>
</tbody>
</table>

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## Process Development for Blended Elemental
### P/M Ti-6Al-4V FRED SERT (IBIF)

### Room Temperature Tensile Properties

<table>
<thead>
<tr>
<th></th>
<th>Ultimate Tensile Strength, ksi</th>
<th>Yield Strength, ksi</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>144.1 – 149.8</td>
<td>140.7 – 143.7</td>
<td>19.4 – 21.2</td>
</tr>
<tr>
<td>Extruded</td>
<td>148.3 – 151.6</td>
<td>142.7 – 145.1</td>
<td>19.8 – 22.8</td>
</tr>
<tr>
<td>AMS 4928R</td>
<td>135 Min.</td>
<td>125 Min.</td>
<td>10 Min.</td>
</tr>
</tbody>
</table>

### Fatigue Test Results

<table>
<thead>
<tr>
<th></th>
<th>Maximum Load (lb)</th>
<th>Maximum Stress (ksi)</th>
<th>Cycles to Failure</th>
<th>Diameter (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>5880</td>
<td>119</td>
<td>1,014,725</td>
<td>0.251</td>
</tr>
<tr>
<td>Extruded</td>
<td>5880</td>
<td>119</td>
<td>3,716,462</td>
<td>0.250</td>
</tr>
</tbody>
</table>

### Microstructures: Extruded Material

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Corrosion Resistant Heat Exchanger and Chemical Process Seamless Tubing Manufacture Directly from Extruded Titanium Powder

ADMA CIP Tooling

ADMA Ti Billets

Centered and Ready for Hot Extrusion

Ready to Pilger

Extruded Tubes
### P/M Ti-6Al-4V CIP/Sinter/Ring Rolling

#### Process Flow
- Cold Isostatic Pressing
- Sintering
- Forging/Ring Rolling

#### Element Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>5.83</td>
</tr>
<tr>
<td>Vanadium</td>
<td>3.96</td>
</tr>
<tr>
<td>Iron</td>
<td>0.15</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.19 – 0.20</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.008</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.015</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0052</td>
</tr>
<tr>
<td>Yttrium</td>
<td>&lt; 0.0005</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.014</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.014</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.013</td>
</tr>
<tr>
<td>Other elements each</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Other elements total</td>
<td>&lt; 0.40</td>
</tr>
<tr>
<td>Titanium remainder</td>
<td></td>
</tr>
</tbody>
</table>

#### Ti-6Al-4V Mechanical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>ADMA PM Ti-6Al-4V</th>
<th>AMS 4928R</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTS, ksi</td>
<td>144 - 148</td>
<td>135 Min.</td>
</tr>
<tr>
<td>YS, ksi</td>
<td>136 - 138</td>
<td>125 Min.</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>14 - 16</td>
<td>10 Min.</td>
</tr>
<tr>
<td>RA, %</td>
<td>29 - 31</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Ultrasonic Inspect
- Ultrasonic Inspect per AMS-STD-2154 Rev. A, Type 1, Class A UT-001 Rev. C

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P/M Ti-6Al-4V ELI Grade Pre-form
Manufactured from ADMA TiH\textsubscript{2} powder

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>5.52</td>
</tr>
<tr>
<td>Vanadium</td>
<td>3.92</td>
</tr>
<tr>
<td>Iron</td>
<td>0.13</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.13</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.012</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0055</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0003</td>
</tr>
<tr>
<td>Yttrium</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.013</td>
</tr>
<tr>
<td>Other elements each</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Other elements total</td>
<td>&lt; 0.15</td>
</tr>
<tr>
<td>Titanium total</td>
<td>remainder</td>
</tr>
</tbody>
</table>
Room Temperature mechanical properties of Ti-1Al-8V-5Fe (Ti185) alloy round bars rolled in both blended-elemental powder-based and ingot-based double-VAR billet product forms.

<table>
<thead>
<tr>
<th>Alloy/Billet Ident.</th>
<th>Specimen ID</th>
<th>Round-Bar Rolling Reduction in Diametral Dimension</th>
<th>Ultimate Tensile Strength [ksi]</th>
<th>0.2% Yield Strength [ksi]</th>
<th>Elongation [%]</th>
<th>Elastic Modulus [Msi]</th>
<th>Fracture Toughness $K_{IC}$ (KQ) [ksi] (inch)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti185 Blended-Elemental Powder-Based Alloy, CIP / Sintered and round-bar rolled</td>
<td>Alloy 1 – T1</td>
<td>4” $\rightarrow$ 1”</td>
<td>201.3</td>
<td>194.6</td>
<td>17</td>
<td>15.2</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>Alloy 1 – T2</td>
<td>4” $\rightarrow$ 1”</td>
<td>205.2</td>
<td>198.4</td>
<td>16</td>
<td>15.4</td>
<td>22.8</td>
</tr>
<tr>
<td>Ti-185 Ingot-Based Alloy Double VAR Round-Bar Rolled</td>
<td>RRR2-T1</td>
<td>4” $\rightarrow$ 1”</td>
<td>201.8</td>
<td>194.0</td>
<td>12</td>
<td>17</td>
<td>34.0</td>
</tr>
<tr>
<td></td>
<td>RRR2-T2</td>
<td>4” $\rightarrow$ 1”</td>
<td>208.0</td>
<td>199.4</td>
<td>10</td>
<td>16.5</td>
<td>31.5</td>
</tr>
</tbody>
</table>
ADMA PRODUCTS, INC. is vertically integrated manufacturer of titanium alloy components.

Titanium alloy components manufactured by our low-cost blended elemental powder metallurgy approach meet the AMS specification mechanical property requirements and exceed the properties obtained on similarly-processed ingot-based titanium products.