Innovative Process for Manufacturing Hydrogenated Titanium Powder for Solid State Production of P/M Titanium Alloy Components

O.M. Ivasishin¹, M.V. Matviychuk¹, C.A. Lavender², G.I. Abakumov³, V.A. Duz³, V.S. Moxson³

1-Institute for Metal Physics, Kiev, Ukraine
2-Pacific Northwest National Laboratory, Richland, WA, USA
3-ADMA Products, Inc. Hudson, OH, USA

© 2010 ADMA
Conventional Titanium Ingot Metallurgy Process

High Cost, High Energy Consumption, High Labor, High Waste

A high “buy-to-fly “ ratio process

Development of new technologies that provide cost-effective manufacturing of titanium alloy components provides expanded application for titanium products.
Conventional Powder Metallurgy

No Significant Cost Reduction Through Conventional Powder Metallurgy Process
Issues that have Hindered Titanium Powder Metallurgy Industry Development

1. Chemistry issues:

   • High Interstitial content – the need to remove Chlorine, Magnesium, Sodium (with ingot metallurgy melting removes interstitials)

   • High oxygen content (related to high surface area of titanium powders, with ingot metallurgy removed by melting)

2. Properties issues:

   • Inferior Low Cycle Fatigue and fatigue related properties, inferior fracture toughness

   • “Weld-ability” Issues

   • P/M Ti alloys did not meet Airspace Material Specifications (AMS)
Global Powder Metallurgy Industry
(Annual - All metals)

$25 Billion (Global)
$5 Billion (USA)

Over 70% to Auto Industry

Source: Metal Powder Industries Federation June 2010
Cooperation (started late 1990’s)

Aimed at development of most cost-effective BEPM press-and-sinter approach for manufacturing titanium components possessing relative density 98-99%, chemical and microstructural homogeneity and mechanical properties to meet commercial demands.

**U K R A I N E**

**TITANIUM INSTITUTE**

Институт Титана

leading organization in titanium R&D in FSU

**INSTITUTE FOR METAL PHYSICS**

basic studies in titanium alloy and process development, Ukrainian team leader

**ZTMK**

one of the largest titanium sponge producer, world leader in hydrogenated titanium

**U S A**

**Pacific Northwest National Laboratory**

R&D in low-cost titanium powder and components manufacturing processes for DOE applications

**Components producer, R&D**

© 2010 ADMA
Titanium Powders Produced by electrolysis in 1990`s

<table>
<thead>
<tr>
<th>Grade</th>
<th>Size, mm</th>
<th>HB, not more than</th>
<th>Ti</th>
<th>Fe</th>
<th>Cl</th>
<th>N</th>
<th>O</th>
<th>C</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>ПТЕК-1</td>
<td>-5+0.6</td>
<td>120</td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
<td>0.06</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>ПТЕК-2</td>
<td>-5+0.6</td>
<td>155</td>
<td>0.10</td>
<td>0.08</td>
<td>0.04</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>ПТЕС-0</td>
<td>-0.63+0.18</td>
<td>100</td>
<td>0.04</td>
<td>0.05</td>
<td>0.03</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>ПТЕС-1</td>
<td>-0.63+0.18</td>
<td>120</td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
<td>0.06</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>ПТЕС-2</td>
<td>-0.63+0.18</td>
<td>155</td>
<td>0.10</td>
<td>0.08</td>
<td>0.04</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>ПТЕМ-1</td>
<td>-0.18</td>
<td>NM*</td>
<td>0.08</td>
<td>0.06</td>
<td>0.03</td>
<td>NM</td>
<td>0.03</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>ПТЕМ-2</td>
<td>-0.18</td>
<td>NM</td>
<td>0.20</td>
<td>0.15</td>
<td>0.05</td>
<td>NM</td>
<td>0.03</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

*NM - not measured

© 2010 ADMA
One of the largest titanium sponge producers and world leader in hydrogenated titanium sponge.
High-Dense (99%) BEPM Titanium Alloys

Employment of TiH$_2$ instead of Ti powder in BEPM allows attainment of 99% density and mechanical properties equivalent to those of ingot materials with most cost-effective press-and-sinter approach (without HIP)

- Specific mechanism of compaction $\rightarrow$ optimized green porosity
- Shear type phase transformation TiH$_2$ $\rightarrow$ Ti (β or α) $\rightarrow$ high density of crystal lattice defects
- Surface self reducing by atomic hydrogen

© 2010 ADMA
Comparison of Ti- and TiH₂-based Blends

TiH₂-based blends

Ti-based blends

Sintered densities of TiH₂ blends:
- do not noticeably depend on molding pressure
- higher than in equivalent Ti-based blends.

© 2010 ADMA
Development of cost-effective technology for manufacturing hydrogenated titanium

Integrated process

Hydrogenated Ti sponge block crushing

Reduction (retort 1m) → Partial vacuum separation of titanium sponge. Cooling → Hydrogenation

MgCl₂ → TiCl₄ → Vacuum (Argon) → Hydrogen

© 2010 ADMA
Production of Hydrogenated Titanium Powders

Requirements:
- Industrial scale - large quantity of powder
- Desirable chemistry (hydrogen and impurity content)
- Sizing
- Affordability

© 2010 ADMA
# Typical Characteristics of Hydrogenated Titanium

<table>
<thead>
<tr>
<th></th>
<th>Cl</th>
<th>Fe</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenated Ti Sponge (ZTMC)</td>
<td>0.050</td>
<td>0.062</td>
<td>0.052</td>
<td>0.008</td>
<td>0.013</td>
<td>0.06-0.08</td>
<td>3.90</td>
</tr>
<tr>
<td>Powder (ADMA)</td>
<td>0.054</td>
<td>0.054-0.073</td>
<td>0.041</td>
<td>0.005-0.008</td>
<td>0.013</td>
<td>0.09-0.10</td>
<td>3.90</td>
</tr>
</tbody>
</table>

TiH$_2$ sponge

TiH$_2$ powder (-100 mesh)

© 2010 ADMA
Easier crushing underseparated shorter time lower energy lower labor

Cost reduction

Cost increasing hydrogenation

Cost of Hydrogenated Powder

Cost of Titanium Sponge

© 2010 ADMA
Components Manufacturing Developed by ADMA

ADMA Titanium P/M “in house” Processes

- Die Press
- Direct Powder Rolling
- Cold Isostatic Pressing
- Vacuum Sintering
- Vacuum Sintering

Post-Processing Outside vendors

- Forging
- Rolling Flat (foil, sheet, plate) Round (bar, rod)
- Extrusion
- Flowform
- HIP

TiH$_2$ + Master Alloy Powder

© 2010 ADMA
Alloy Synthesis Strategy Developed by IMP

Optimized condition:
- chemical (microstructure) homogeneity
- low volume fraction, spherical shape and minimized size of pores
- fine beta grains
- low impurity content

Chemical and microstructural homogenization

Healing of pores

Grain growth
(depending on volume fraction, size and morphology of pores)

\[ L_{av} \approx \frac{R_{av}}{\theta} \]

- \( L_{av} \): average grain size
- \( R_{av} \): average pore size
- \( \theta \): porosity

Synthesis temperature and time

© 2010 ADMA
Diffusion of Alloying Elements in Titanium

- Diffusion determines chemical homogenization and sintering of powders
- Peculiarities of alloy synthesis depend on its composition
Dilatometry

- Indication that impurities and alloying elements affect powder metallurgy processing
Anomalous Grain Growth
## Example of Alloys Sintered from Hydrogenated Titanium Powder

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Density, %</th>
<th>YS, MPa</th>
<th>UTS, MPa</th>
<th>El., %</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>99</td>
<td>875-877</td>
<td>944-951</td>
<td>11.8-13.1</td>
<td>33.2-38.2</td>
</tr>
<tr>
<td>ASM specification</td>
<td></td>
<td>≥ 828</td>
<td>≥ 897</td>
<td>≥ 10</td>
<td>≥ 20</td>
</tr>
<tr>
<td>Ti-5Al-5V-5Mo-3Cr</td>
<td>98.5</td>
<td>1200</td>
<td>1304</td>
<td>6.8</td>
<td>10.3</td>
</tr>
<tr>
<td>BMS 7-360 Specification. High strength condition</td>
<td>1170</td>
<td>1240</td>
<td>5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ti-10V-2Fe-3Al</td>
<td>98</td>
<td>1115</td>
<td>1250</td>
<td>5.2</td>
<td>11.0</td>
</tr>
<tr>
<td>AMS 4984 Specification. High strength condition</td>
<td>1103</td>
<td>1193</td>
<td>4</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Gas impurities: Oxygen: 0.13-0.18%, Hydrogen 0.002-0.003%

© 2010 ADMA
Inherent Issues Related to
-hydrogen
-oxygen
-chlorine
-master alloy powders
Hydrogen

1 kg TiH₂ → 40 g or 448 liters of H₂

- high capacity pumping system required
- heating rate/hydrogen pressure control is necessary for proper processing
Oxygen

- Excessive oxygen content in synthesized alloys leads to increased strength but low ductility or even brittleness.

Sources of contamination:
- Starting base powder (typically 0.10-0.15 wt.%),
- Alloying powders (up to 1 wt.%),
- Processing (blending, compaction, sintering procedures).

Hydrogenated powder 0.15 wt.%
Green compact Ti-6Al-4V 0.26 wt.%
Ti-6Al-4V alloy 0.11 wt.%

Final oxygen content is generally lower than in green compacts due to hydrogen’s reducing effect.
Low-oxygen P/M Ti-6Al-4V Billets from Hydrogenated Ti Powder

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>H09-02-25.1/01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>.143%</td>
</tr>
<tr>
<td>Carbon</td>
<td>.009%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>.012%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>.0275 %</td>
</tr>
<tr>
<td>Aluminum</td>
<td>6.01%</td>
</tr>
<tr>
<td>Vanadium</td>
<td>4.12%</td>
</tr>
<tr>
<td>Iron</td>
<td>.085%</td>
</tr>
<tr>
<td>Yttrium</td>
<td>.0008%</td>
</tr>
<tr>
<td>Chromium</td>
<td>.022%</td>
</tr>
<tr>
<td>Nickel</td>
<td>.024%</td>
</tr>
<tr>
<td>Silicon</td>
<td>.016%</td>
</tr>
<tr>
<td>Total others</td>
<td>&lt;.40%</td>
</tr>
<tr>
<td>Titanium</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

Ti-6Al-4V billet 8.50” x 12.0” x 52.0” 725 lbs

© 2010 ADMA
Chlorine

Starting chlorine content 0.10% in sponge reduced to 0.08% during sponge hydrogenation and further during sintering providing sufficient mechanical properties.

Final alloy:
Cl: 0.015%
O: 0.112%
N: 0.024%

<table>
<thead>
<tr>
<th>YS, MPa</th>
<th>UTS, MPa</th>
<th>El., %</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>905</td>
<td>946</td>
<td>11.5</td>
<td>35.8</td>
</tr>
</tbody>
</table>

© 2010 ADMA
Master Alloy Powders

- MA/titanium matrix interface affects shrinkage
- MA particle size distribution affects residual porosity
Conclusion

Cooperation proved successful in the development of a new titanium powder metallurgy process. More details as to the results under the hydrogenated titanium powder process will be presented by our next speaker.