Extra Low Impurity Content Powder Metallurgy Titanium and Titanium Alloys

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Professor Ivasishin, Director of IMP, IMP
October 7-10, 2012 • Atlanta, Georgia, USA
What hinders titanium powder metallurgy industry development?

Chemistry issues:

High oxygen content (related to high surface area of titanium powders) - 0.20% O max per AMS 4928L
Need to remove Chlorine, Magnesium, Sodium (only melting can remove impurities)

Properties issues:

Inferior low cycle fatigue, fatigue related properties, and fracture toughness

Weldability issues
Introduction: Role of Impurities in Ti PM

Chlorine

Problems related to impurities:
- Brittleness;
- Low fracture toughness

(F.Froes, D.Eylon, 1990)

Inherent porosity
- Reduced fatigue properties
- Weldability issues
Impurities in PM Produced Articles

Impurities in starting powders:
- locate on powder surface
- depend on particle size

Contamination upon processing:
- grinding
- blending
- compaction
- exposures between processing steps
- sintering

Final impurity content

To obtain allowable impurity content in final BEPM alloys and articles:
- high purity powders are required
- protection from contamination upon processing is extremely important
Powder Quality/Size/Cost Relationship

P – cost of low grade titanium powder

T. Saito, 2006 (modified)
Development and Patenting

Institute for Metal Physics (Ukraine) and ADMA Products, Inc. (USA) have jointly developed the approach based on application of hydrogenated titanium powder as starting material for BEPM

• Ukraine patents No 65654, 70366, 92714
• US Patents No 6638336B1, 7993755
• International Patent Application No. PCT/US 2012/045170 filed 03-08-2012
ZTMC Hydrogenated Titanium Powder (TiH₂)

- Low impurity content
- Cost effective
- Technologically attractive (easy grinding, low adhesion to die walls)
- Increased shelf life

Typical composition of hydrogenated titanium produced at Zaporozhje Ti&Mg Combine (ZTMC), Ukraine

<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 sponge</td>
<td>0.05</td>
<td>0.062</td>
<td>0.052</td>
<td>0.008</td>
<td>0.013</td>
<td>0.06</td>
<td>3.85</td>
</tr>
<tr>
<td>Powder -100 μm</td>
<td>0.054</td>
<td>0.054-0.073</td>
<td>0.041</td>
<td>0.005-0.008</td>
<td>0.011-0.013</td>
<td>0.09-0.10</td>
<td>3.9</td>
</tr>
</tbody>
</table>
ADMA Hydrogenated Powder

* Average from over 20 production runs

<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>
Typical Impurities

Ti 2p Spectra

Al source gives information about surface layer

mono Al source (hv = 1486.74 eV)

mono Ag source (hv = 2984.3 eV)

Ag source gives information about deeper layers
O 1S Spectra

Al source gives information about surface layer

Ag source gives information about deeper layers
Oxygen in Powder Particles

O 1S spectra

Two states of oxygen:
- TiO₂
- H₂O

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Two states of oxygen:
- TiO₂
- H₂O
Substitution of TiH$_2$ powder for Ti powder permits decreasing contamination titanium refinement.
How to Decrease the Contamination?

- Transformation of the impurities into volatile products

High-temperature dilatometer combined with mass-spectrometer
Reduction of Oxygen Content

Desorption of moisture

Reduction of surface TiO₂

TiO₂ + 4H = Ti + 2H₂O

H₂O emission within dehydrogenation interval proves refinement of material from O with hydrogen
Emission of HCl and C-H compounds within dehydrogenation interval proves refinement of material from C and Cl with hydrogen.
How to Decrease the Contamination?

- Transformation of the impurities into volatile products
- Allow volatile products to get out from the articles - open porosity is necessary
How to Decrease the Contamination?

- Transformation of the impurities into volatile products
- Allow them to get out from the articles - open porosity is necessary
- Competitive process, e.g. dissolution of surface impurities in bulk titanium should be avoided

Reduction of surface oxide scales has to be realized before their dissolution
How to Decrease the Contamination?

- Transformation of the impurities into volatile products
- Allow them to get out from the articles - open porosity is necessary
- Competitive process, e.g. dissolution of impurities in titanium should be avoided

Gases (H₂O) Emission

- Oxygen
  $$\text{TiO}_2 + 4\text{H} = \text{Ti} + 2\text{H}_2\text{O}$$

- Chlorine
  $$\text{MgCl}_2 + 2\text{H} = \text{Mg} + 2\text{HCl}$$

Temperature

Dissolution of impurities

Open porosity

Closed porosity
Pressure Condition upon Dehydrogenation

Hydrogen and other gases emitted should be evacuated from the furnace in due temperature interval

Balance

Rate of hydrogen release  Rate of hydrogen pumping out
Dehydrogenation Kinetics

Important parameters:
- Particle size
- Heating rate
- Vacuum degree

Time of dehydrogenation depends on particle size \( r \)

\[
\tau = \frac{r^2}{\pi^2 D} \ln \left( \frac{C_0 - C_p}{C - C_p} \right)
\]

Fast heating, large particles, excess hydrogen partial pressure

Slow heating, small particles, high vacuum
## Typical Laboratory Experiments: Content of Impurities

<table>
<thead>
<tr>
<th>Impurities</th>
<th>Oxygen Content</th>
<th>Chlorine Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiH$_2$ powder</td>
<td>0.16%</td>
<td>TiH$_2$ powder</td>
</tr>
<tr>
<td>Green compact Ti-6Al-4V</td>
<td>0.26%</td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-4V alloy</td>
<td><strong>0.11%</strong></td>
<td>Ti-6Al-4V Alloy</td>
</tr>
</tbody>
</table>

**Final carbon content:** 0.05-0.07%

**Final hydrogen content:** 0.002-0.003%
Production of Large CIP-Sinter Preforms

Ti-6Al-4V composition

Weight of compacted preforms: up to 340 kg (750 lbs)
Dehydrogenation Kinetics

Important parameters:
- Particle size
- Heating rate
- Vacuum degree

Time of dehydrogenation depends on particle size $r$

$$\tau = \frac{r^2}{\pi^2 D} \ln \frac{C_0 - C_p}{C - C_p}$$

- Slow heating, small particles, high vacuum
- Fast heating, large particles, excess hydrogen partial pressure
Pressure Condition upon Dehydrogenation

Balance

Rate of hydrogen release  Rate of hydrogen pumping out

TiH\textsubscript{2} contains 4% H by weight
340 kg → 13.6 kg H → 152.3 m\textsuperscript{3} hydrogen
First industrial trials

- low rate of hydrogen and other gases evacuation from sintering chamber
- excess amount of gas impurities in CIP/Sintered/Extruded Ti-6Al-4V material compare to requirements of AMS specifications
- reduced fracture toughness and stress corrosion resistance as well as faster fatigue crack growth rates as compared to ingot material

<table>
<thead>
<tr>
<th></th>
<th>Oxygen, %</th>
<th>Hydrogen, %</th>
<th>YS, MPa</th>
<th>UTS, MPa</th>
<th>El., %</th>
<th>Fracture tough., MPa m$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIP-Sintered billet</td>
<td>0,29</td>
<td>0,0480-0,1000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Extrusions</td>
<td>0,29</td>
<td>0,0417</td>
<td>926</td>
<td>1022</td>
<td>15,4</td>
<td>56/43</td>
</tr>
</tbody>
</table>

After Redesign of Vacuum System

More powerful pumping system provided faster evacuation of gases emitted

<table>
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<th>Hydrogen, %</th>
<th>YS, MPa</th>
<th>UTS, MPa</th>
<th>El., %</th>
<th>Fracture tough., MPa m^{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIP-Sintered billet</td>
<td>0.18</td>
<td>0.0270</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Extrusions</td>
<td>0.19</td>
<td>0.0097</td>
<td>876</td>
<td>979</td>
<td>13</td>
<td>76/61</td>
</tr>
</tbody>
</table>

Weldability

Characteristics of CIP/Sintered/Hot deformed plates

<table>
<thead>
<tr>
<th>Composition</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>H</th>
<th>Cl</th>
<th>Mg</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>6.16</td>
<td>4.21</td>
<td>0.080</td>
<td>0.010</td>
<td>0.010</td>
<td>0.179</td>
<td>0.0054</td>
<td>&lt;0.0010</td>
<td>0.0016</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Low chlorine content in produced articles implies sufficient weldability characteristics.

Preliminary tests were successful.
Conclusions

- Using of high purity hydrogenated powder and optimization of sintering process resulted in production of titanium components with low interstitial content that easily meet ASTM and AMS requirements.

- Laboratory experiments allowed development of physical background of the refinement of BEPM titanium products from O, Cl and C impurities by hydrogen released from the titanium hydride.

- Optimization of heating conditions in vacuum furnace allowed decrease of impurity content in industrial scale TiH$_2$-based preforms.

- Ti-6Al-4V preforms with low impurity content were produced and used for manufacturing products with high balance of mechanical properties.
Thank You for Your Attention