ADMA Pilot Plant for Hydrogenated Titanium Powder Production

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Presentation overview

ADMA innovative process for manufacturing of Titanium and Titanium hydride (TiH2) powder

Advantages of ADMA Process compare to conventional processes:

• Decreasing of consumption of magnesium in reduction process
• Decreasing of energy consumption in vacuum separation process (with at least triple production output)
• Positive effect of hydrogen in reducing overall duration of process time (cycle is reduced from 180 to 24-48 hours)
• Decreasing of labor cost (up to 60%) compare to traditional Kroll process

ADMA development activities to produce the low-cost titanium
ADMA Products, Inc. R&D Facility, Hudson, OH

20,000 SF

In 2010 ADMA received $1.4M Congressional award under the 2009 Defense Appropriations Act to begin production of hydrogenated titanium powder in the USA.
ADMA Products, Inc. Titanium Powder Production, Twinsburg, OH

2 Buildings - 41,200 SF

Pilot scale unit for hydrogenated titanium powder production (660 lbs/run)

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ADMA Process for TiH\textsubscript{2} powder manufacturing


Traditional Kroll process:

\[
\text{TiO}_2 \rightarrow \text{TiCl}_4 \rightarrow (+\text{Mg}) \rightarrow \text{Ti (sponge)}
\]

ADMA process adds H\textsubscript{2} in different stage of process and in different forms

\[
\text{TiO}_2 \rightarrow \text{TiCl}_4 \rightarrow (+\text{H}_2) \rightarrow \text{TiCl}_3 \rightarrow (+\text{Mg}) \rightarrow (+\text{H}_2) \rightarrow \text{TiH}_2(\text{powder})
\]

Before the reduction process: \(
\text{TiCl}_4 + \text{H}_2 (\text{gas}) \rightarrow \text{TiCl}_3 + \text{HCl}
\)

In the reduction process:

\[
\text{TiCl}_3 + \text{H}_2 (\text{gas} + \text{solid in TiH}_x + \text{solution in molten Mg}) + \text{Mg} \rightarrow \text{TiH}_2 (s) + \text{MgCl}_2
\]

In process only hydrogen H\textsubscript{2} is added

H\textsubscript{2} – recycling in H\textsubscript{2} (gas) and HCl (gas)
Hydrogen H$_2$ in ADMA technology
advantages over conventional technologies

Reduce consumption of magnesium Mg using TiCl$_3$ instead of TiCl$_4$ in reduction process
TiCl$_4$ +H$_2$ -> TiCl$_3$ + HCl

Intensification of mass transfer processes in reduction of titanium chlorides by
Mg {H}, TiH$_2$ (solid), H$_2$ (gas)

Intensification of heat transfer processes during vacuum separation due to the high thermal conductivity of hydrogen

Decreasing of vacuum separation time due to the destruction of closed pores in the titanium sponge

Crushing of brittle TiH$_2$ to powder directly in the retort, and removal of powder by Ar pneumatic

Intensification of sintering due to the absence of oxide film on the surface of the powder, removing chlorine and oxygen by atomic hydrogen
Hydrogen reduces consumption of magnesium

TiCl₄(liquid) + H₂(gas) → TiCl₃(solid) + HCl(gas)

Hydrogen H₂ (by t= 500 C) reduces TiCl₄ to TiCl₃ and decreases consumption of magnesium Mg in next process

TiCl₄ + 2Mg = Ti + 2MgCl₂
1 kg Ti = 1 kg Mg

2 TiCl₃ + 3 Mg = 2Ti + 3 MgCl₃
1 kg Ti = 0.75 kg Mg + 0.02 kg H₂
Intensification of mass transfer processes in the reduction cycle

MgCl₂ → TiCl₄

Kroll process

ADMA process

TiCl₄ (liquid)

TiCl₃ (solid)

H₂ (gas)

TiH₂ (solid) 1-3%

TiH₂ → Ti + H₂↑ (bubbles)

Bubbles float up, mixing the liquid phase of Mg and MgCl₂ and accelerating reduction process

Mg + H₂ → Mg [H] (solution)

Ti + H₂ + [H] → TiHₓ (t=780-850°C)

TiCl₄ + H₂ → TiCl₃ + HCl

HCl + Mg → MgCl₂ + H₂↑

Hydrogen transfer accelerates reduction process
Intensification of heat transfer processes during vacuum separation stage

Intensification of **heat transfer** processes during vacuum separation due to high thermal conductivity of hydrogen

**Heat transfer in Kroll process:**
1. thermal radiation
2. heat conduction through the walls of titanium pores

**ADMA process**
1. thermal radiation
2. heat conduction through the walls of titanium pores
3. heat conduction through hydrogen $H_2$ (at times)
4. convection heat transfer by $H_2$ (at times)
Reducing energy expenditure in vacuum separation cycle

Decreasing of vacuum separation time due to the destruction of closed pores in titanium sponge by hydrogenation–dehydrogenation process

\[
\text{Ti + H}_2 \rightarrow \text{TiH}_2 \quad (\text{TiH}_2 \text{ density } 3.75 \ t/m^3)
\]

\[
\text{TiH}_2 \rightarrow \text{Ti} + \text{H}_2 \quad (\text{Ti density } 4.5 \ t/m^3)
\]

\[\Delta V = 18\%\]
therefore closed pores are opened
Grinding of brittle TiH$_2$ sponge directly in the retort

![Graphs showing size distribution and percentage of material by size over 30 and 120 seconds.]

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TiH₂ sponge and powder

TiH₂ sponge in block

TiH₂ powder

O₂ content from run to run

H₂ content from run to run

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ADMA development activities.
Alloying of titanium hydride powder in the retort

Advantages of alloying in the retort:
1. The ability to create any mixture of components without introducing oxygen into the process
2. The uniform distribution of elements with content of less than 0.01% (using mixing in liquid titanium tetrachloride)
3. Preparation of alloys with 8-10 alloying elements (different density and content) with good homogenization
4. Reduced cost of alloys using the low-cost chlorides of alloying elements

Methods of alloying
1) Using of standard master alloy powder
2) Using of liquid chlorides and bromides of alloying elements
3) Using of gas phase of chloride of alloying elements
4) Using of elements dissolved in the magnesium (aluminum Al, nickel Ni)

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Alloying of titanium hydride powder in the retort

Alloy Ti-3Al-2V (after addition of Al-V master alloys powder and titanium hydride in liquid TiCl4 during reduction cycle)

<table>
<thead>
<tr>
<th>Element in alloys</th>
<th>The compound does not increase oxygen content in Titanium alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Al- solution in Mg AICl3 (s); AlBr3 (l)</td>
</tr>
<tr>
<td>V</td>
<td>VCl4 (l);VCl3 (s)</td>
</tr>
<tr>
<td>Mo</td>
<td>MoCl5 (s)</td>
</tr>
<tr>
<td>Cr</td>
<td>CrCl2 (s), CrCl3 (s)</td>
</tr>
<tr>
<td>Fe</td>
<td>FeCl2 (s), FeCl3 (s)</td>
</tr>
<tr>
<td>Zr</td>
<td>ZrCl4 (s)</td>
</tr>
<tr>
<td>Nb</td>
<td>NbCl5 (s)</td>
</tr>
<tr>
<td>Mn</td>
<td>MnCl2 (s)</td>
</tr>
<tr>
<td>Sn</td>
<td>SnCl4 (l) SnCl2 (s)</td>
</tr>
</tbody>
</table>

Increasing of oxygen content in Ti-6Al-4V alloy due to the oxide film on master alloys powder (calculation)

<table>
<thead>
<tr>
<th>The specific surface of the powder alloy elements m2 / g</th>
<th>The thickness of oxide film is 20 nm</th>
<th>0.1 m2/g</th>
<th>0.035 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 m2/g</td>
<td></td>
<td></td>
<td>0.35 %</td>
</tr>
</tbody>
</table>
“ADMA-TiH2” technology can be easy integrated into the structure of existing Titanium sponge production plants

The chlorination process slightly modified (TiCl3 instead of TiCl4)

The reduction process will retain its structure, but magnesium consumption reduced by use of hydrogen

The magnesium chloride electrolysis will remain unchanged.

Sponge crushing and sorting is completely eliminated

Hydrogen, chlorine and magnesium are recycled in the process

only hydrogen H2 is added
Production unit for hydrogenated titanium powder production (5,000 lbs/run)
CONCLUSIONS

1. An innovative process for manufacturing of the hydrogenated titanium powder (TiH₂) has been developed

2. Use of hydrogen at all stages of the process (from the production of titanium tetrachloride to sintering) can significantly reduce energy consumption and process time, and thus reduce the cost of titanium products

3. A pilot scale unit with a capacity of 660 lbs/run for TiH₂ powder production has been installed and operates at the ADMA facility (Twinsburg, OH)

4. The future plans – to design and build a full scale TiH₂ powder production plant with annual capacity of 45 mln pounds