Production of Titanium Alloys with Exceptional Mechanical Properties by Hydrogen Sintering and Phase Transformation (HSPT)

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Outline

• Motivation
• Description of the process
  – Powder, compaction, and sintering
• Key advantages and characteristics
• Microstructure and mechanical properties
  – Effect of process parameters (T, $p_{H_2}$, etc.)
• Comparative energy analysis
• Conclusion
Motivation

Superior Performance of Titanium

- **Performance**
  - High specific strength, excellent ductility, corrosion resistance

- **Cost and efficiency of current processing**
  - The buy to fly ratio of Ti parts in the F-22 program was poor with a 92% scrap content

Powder Metallurgy vs. Wrought Processing

- **Cost promises of titanium P/M**
  - Near net shape manufacturing, direct use of scrap materials, etc.

- **Inferior properties compared to wrought titanium**
  - Poor strength, ductility, and fatigue properties from resulting P/M microstructure – requires further processing

Cost bread down to produce 1” thick titanium plate using traditional processing

A new P/M process

Sponge Ti

Sponge Hydrogenation

TiH₂ Powder

Compaction and sintering

Ti Powder

Major thermal mechanical working: Forging, Rolling, Milling, Extrusion

Milled Products

Secondary cold or hot mechanical working: forging, extrusion, etc

Shaped products: rods, bars, plates

Final products

James Paramore, PhD Candidate
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Powder

- PM of titanium is notoriously difficult due to oxygen contamination of the highly reactive titanium powder surfaces
  - Oxygen at particle surfaces mitigates densification, resulting in porous microstructure with poor mechanical properties
  - Oxygen in bulk metal is detrimental to mechanical properties
- TiH$_2$ is stable in atmosphere at room temperature, all but eliminating oxide contamination during handling and storage of hydride powders
- Compaction and green machining of TiH$_2$ powders
- Unreactive hydride in – corrosion resistant metal out... no special processing required

Equilibrium pressure of H$_2$ over TiH$_2$ as a function of temperature
Due to TiH₂ brittleness, the powder “crushes” at high pressure, meaning exceptionally high green densities and strengths are obtainable.
Sintering

0.01 atm $< p_{H_2} < 0.2$ atm

INERT GAS BALANCE

Improved densification due to rapid self diffusion and weak Ti-H bonds in $\beta$-Ti(H) phase

Eutectoid decomposition breaks up and refines microstructure

$\beta$-Ti(H) $\Rightarrow (\alpha+\beta) + 3$ TiH$_2$

Dehydrogenation removes remaining hydrogen far below ASTM standards

$3$ TiH$_2$ $\Rightarrow \alpha + \beta$
Key advantages of HSPT

- **Unreactive nature of TiH$_2$**
  - TiH$_2$ will not spontaneously oxidize in atmosphere
    - Better powder purity
    - No need for exotic handling procedures
    - SAFETY!

- **Improved densification**
  - Compaction behavior of TiH$_2$ is exceptional
  - Ti-H bonds weaker than Ti-Ti bonds
  - Improved self diffusion of Ti $\rightarrow$ increased densification kinetics

- **Microstructural control**
  - Eutectoid decomposition of $\beta$ grains $\rightarrow$ grain refinement
  - Degree of grain refinement is a function of p$_{H2}$
    - Application tailored microstructure/mechanical properties
Microstructure

Vacuum Sintered Ti
- Poor densification
- Coarse microstructure

Vacuum Sintered TiH$_2$
- Significantly improved densification
- Coarse microstructure

HSPT Sintered TiH$_2$
- Excellent densification
- Unprecedented microstructural control
Microstructure

- High magnification metallography reveals nano-sized features
- Size and morphology of these features is dependent on process parameters
- Possibility to tailor mechanical properties to applications
Mechanical Properties

- Process seems to be tolerant of high oxygen levels
- Possibility to easily increase strength but retain ductility

<table>
<thead>
<tr>
<th>ASTM B348 Wrought Standard</th>
<th>UTS (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 5 (Ti-6Al-4V)</td>
<td>895</td>
<td>828</td>
<td>10</td>
</tr>
</tbody>
</table>

YS: 895; UTS: 967 MPa; El.: 15%

YS: 1010; UTS: 1105 MPa; El.: 15%
Effect of Eutectoid Decomposition Temperature

Eutectoid decomposition kinetics are strongly dependent on $T$ and $H$ concentration during transformation.

As concentration of hydrogen increases, the nose temperature decreases, and the nose time increases (kinetics slow).

Example: If one was to treat a Ti-6-4 sample containing 20at% H at 750°C, even though the hold temperature is below the $\beta$-transus, 4 hours is insufficient for the transformation to even start. Whereas, if the sample was treated at 650°C, the reaction is complete after 4 hours.

Maximizing Reaction Kinetics

H concentration changes as a function of temperature for a given $p_{H_2}$

Additionally, the nose temperature for decomposition changes as a function of H concentration

For a given $p_{H_2}$, the intersection between these two curves is the temperature that corresponds to the fastest decomposition kinetics.
Microstructure Versus Eutectoid Decomposition Temperature

If decomposition temperature is too high or too low, grain refinement is compromised.

It is possible this results from thermodynamic as well as kinetic causes.
Energy Analysis

HSPT was modeled using theoretical energy calculations for compaction and sintering

\[
\rho = \rho_0 + AP^{1/3}
\]

\[
E_{\text{compaction, theo}} = \int P \, dV = -\int_{\rho_{\text{loose}}}^{\rho_{\text{green}}} \frac{(\rho - \rho_0)^3}{A^3 \rho^2} \, d\rho
\]

\[
E_{\text{sinter, theo}} = \int_{25^\circ\text{C}}^{T_{\text{sinter}}} C_{p,\text{TiH}_2} \, dT + \Delta H_{\text{TiH}_2 \rightarrow \text{Ti} + \text{H}_2}
\]

Actual energy was then calculated by analyzing sources of energy loss (insulation efficiency, hydraulic efficiency, heat capacity of gases and furnace hardware, etc.)

\[
E_{\text{compaction}} = \frac{E_{\text{compaction, theo}}}{\eta_{\text{hydraulic}}}
\]

\[
E_{\text{sinter}} = \frac{P_{\text{ramp}} + P_{\text{dehydro}} + P_{\text{gas}} + P_{\text{insulation}}}{\mu_{\text{parts}}}
\]
Energy Analysis

Wrought processing was modeled using theoretical energy calculations for double VAR and 8 passes of forging.

\[ E_{VAR,\text{theo}} = 2 \left( \int_{25^\circ C}^{1670^\circ C} C_{p,Ti} dT + \Delta H_{\text{fusion,Ti}} \right) \]

\[ E_{forge,\text{mech, theo}} = \int_{r_i}^{r_f} F dr = \int_{r_i}^{r_f} \frac{2PV}{r} dr = 2PV \ln \left( \frac{r_f}{r_i} \right) \]

\[ E_{VAR} = \frac{E_{VAR,\text{theo}}}{\eta_{VAR}} \quad E_{forge,\text{mech}} = \frac{E_{forge,\text{mech, theo}}}{\eta_{\text{hydraulic}}} \quad E_{forge,\text{heat}} = \frac{E_{forge,\text{heat, theo}}}{\eta_{\text{furnace}}} \]

Theoretical forging calculations were adjusted using literature values for VAR, forging furnace, and hydraulic efficiencies.
Energy Analysis

Results

- Calculations are for 2” round bar stock of Ti-6Al-4V
- 82% energy production savings per ton over wrought processing

<table>
<thead>
<tr>
<th>Component</th>
<th>Electricity (kWh/ton)</th>
<th>Fuel (kWh/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compaction (kWh/ton)</td>
<td>3.93</td>
<td>0</td>
</tr>
<tr>
<td>Compaction Yield</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sintering (kWh/ton)</td>
<td>0</td>
<td>1,667.27</td>
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<tr>
<td>Sintering Yield</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total Energy</td>
<td>3.93</td>
<td>1,667.27</td>
</tr>
<tr>
<td>Coal Equiv. (ton_{Coal}/ton_{Ti})</td>
<td>0.00197</td>
<td>0.27</td>
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</tbody>
</table>

**Total Equiv. Coal (ton_{Coal}/ton_{Ti})** 0.27

<table>
<thead>
<tr>
<th>Component</th>
<th>VAR (kWh/ton)</th>
<th>Forg. (kWh/ton)</th>
<th>Coal Equiv. (ton_{Coal}/ton_{Ti})</th>
<th>Total Equiv. Coal (ton_{Coal}/ton_{Ti})</th>
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</thead>
<tbody>
<tr>
<td>VAR</td>
<td>1,948.79</td>
<td>88.46</td>
<td>0.0136</td>
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<td>VAR Yield</td>
<td>1</td>
<td>0.75</td>
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<tr>
<td>Forging (kWh/ton)</td>
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<td>600.42</td>
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<tr>
<td>Forging Yield</td>
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<td>0.75</td>
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<tr>
<td>Total Energy</td>
<td>2,716.32</td>
<td>800.56</td>
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**Wrought Processing**
Conclusion

• HSPT is a new P/M process to produce Ti alloys with mechanical properties that exceed ASTM standards
  – Consistently produces Ti-6Al-4V with >1 GPa tensile strength and >15 % elongation
• TiH₂ powder is stable in atmosphere and has excellent compaction characteristics
  – Better purity without need for exotic powder handling procedures
  – Possibility of green machining without binders
• Densification kinetics from TiH₂ are significantly faster than Ti
  – >99% density without the need for pressure assisted sintering or post-processing
• Degree of grain refinement during eutectoid decomposition may be controlled by adjusting sintering parameters
  – By controlling T and pₜH₂ during sintering, a wide variety of microstructures are possible
  – Application tailored microstructures and mechanical properties in AS-SINTERED state
• Comparative energy model predicts 80% energy savings over wrought processing to produce 2” round bar stock
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Questions?
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