Hydrogen-induced defects in titanium

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Hydrogen + defects in Ti

Ti and Ti alloys
• high specific strength, stiffness, corrosion resistance

Hydrogen absorbed in Ti
• lowers formation energy of defects (vacancies, dislocations)
• bonded to defects and blocks their movement

Hydrogen-assisted cracking
• degradation of mechanical properties due to absorbed hydrogen
• study of interaction of hydrogen with defects required
**Ti-H system**

- **α-Ti (hcp)**
  - "low" temperature phase

- **β-Ti (bcc)**
  - "high" temperature phase

- **δ-TiH₂ (fcc)**
  - formed at high temperature
  - stabilizes β-phase metastable at room temperature
  - γ-phase is not formed (!)

- **Phase Transitions**
  - $\alpha \rightarrow \beta$ ($\beta \rightarrow \alpha$): lattice deformation (dislocations)
  - $\alpha \rightarrow \delta$ ($\beta \rightarrow \delta$): dislocations + hydrogen induced vacancies
**Hydrogen loading**

**gas loading**
(high temperature, low pressure)
500°C, 0.6 bar H₂
→ complete transformation

**gas loading**
(lower temperature, high pressure)
150°C, 103 bar H₂
→ incomplete transformation

**electrochemical loading**
(local high pressure)
20°C, 20 mA, H₃PO₄ + glycerol (1:1)
→ concentration gradient
XRD – electrochemically loaded Ti

annealed Ti
1000°C / 2 hr in vacuum (10⁻³ mbar)
microstrain (α) \(< 0.8 \times 10^{-4}\)

 electrochemically loaded Ti
(side covered during H loading)
20°C, 20 mA, 239 h
microstrain (α) \(8.8(9) \times 10^{-4}\)

peak broadening analysis
→ microstrain
⇒ high density of dislocations
**XRD – electrochemically loaded Ti**

**electrochemically loaded Ti**
(side exposed to H)
20°C, 20 mA, 239 h
microstrain ($\delta$) \(57(9) \times 10^{-4}\)

**electrochemically loaded Ti**
(side covered during H loading)
20°C, 20 mA, 239 h
microstrain ($\alpha$) \(8.8(9) \times 10^{-4}\)

peak broadening analysis
\(\rightarrow\) microstrain
\(\Rightarrow\) high density of dislocations
XRD – gas loaded Ti

Gas loaded Ti
500°C, 0.6 bar H₂, 10 hours
Microstrain (α) 18(2) x 10^{-4}
Microstrain (δ) 7.8(2) x 10^{-4}
H/Ti ratio 1.2(1)

Gas loaded Ti
500°C, 0.6 bar H₂, 60 hours
Microstrain (δ) 27(2) x 10^{-4}
H/Ti ratio 2.0(2)

Peak broadening analysis
→ Microstrain
⇒ High density of dislocations
Phase analysis + weight change
→ H/Ti ratio
gas loaded Ti
150°C, 103 bar H₂, 4 days
microstrain (α) 16(2) x 10⁻⁴
microstrain (δ) 69(2) x 10⁻⁴
H/Ti ratio 1.7(1)

phase analysis + weight change
→ H/Ti ratio

peak broadening analysis
→ microstrain
⇒ high density of dislocations

gas loaded Ti
500°C, 0.6 bar H₂, 60 hours
microstrain (δ) 27(2) x 10⁻⁴
H/Ti ratio 2.0(2)
XRD analysis - example

phase analysis

- lattice parameters
  \( \alpha \)-Ti \( a = 0.29468(1) \) nm  
  \( c = 0.46791(3) \) nm
  \( \delta \)-TiH\(_2\) \( a = 0.44144(2) \) nm

- volume fraction of \( \delta \)-TiH\(_2\)
  H/Ti ratio 1.7(1)

peak broadening analysis

\( \alpha \)-Ti microstrain 16(2) \( \times 10^{-4} \)
\( \delta \)-TiH\(_2\) microstrain 69(2) \( \times 10^{-4} \)

\( \Rightarrow \) high density of dislocations
Lattice parameter vs. H/Ti ratio

The lattice parameter of $\delta$-TiH$_x$ vs. H/Ti ratio follows the dependence described by Millenbach and Givon [1].

Defect-free Ti – lifetime, HV

- Ti annealed 1000°C / 2 h → single component LT spectrum 144.6(6) ps
- Ti annealed 550°C / 2 h → single component LT spectrum 145.0(8) ps
- bulk hcp α-Ti → ab-initio (LDA) calculated lifetime 146.8 ps
• annealed Ti – single LT component of free positrons $\approx 145$ ps

• cold rolled Ti – saturated trapping at dislocations with lifetime $172(3)$ ps
• transformation $\alpha \rightarrow \delta$ introduces dislocations into the sample
LT results – H-loaded Ti

- **vacancy agglomeration** into clusters:
  - vacancy diffusion SLOW (vacancy formation rate HIGH)

- **vacancy annihilation** in sinks at dislocations and grain boundaries:
  - vacancy diffusion FAST (vacancy formation rate LOW)

**Notes:**
- Low temperature or large loading current
- High temperature or small loading current

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**Graphs:**
- Lifetime (ps) and intensity (%)
- Data points for different conditions (temperature, loading current, pressure)

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Lifetime of vacancy clusters in $\alpha$-Ti

ab-initio calculated lifetime of vacancy clusters in $\alpha$-Ti [2]

ROUGH estimation of mean cluster size:
- clusters in $\alpha$-Ti, not $\delta$-TiH$_2$
- clusters not surrounded with hydrogen atoms

Micrographs of gas-loaded samples

- Growing hydride → lattice expansion → visible cracks → dislocations → hardness enhancement

0.6 bar, 500°C, 10 h

- HV 248(2)

0.6 bar, 500°C, 60 h

- HV 106(3)

- HV 163(4)

Unloaded sample

- HV 155(3)

103 bar, 150°C, 4 d

- HV 221(4)

103 bar, 150°C, 4 d (detail)

Incomplete transformation at low temperature

Smaller hardness of hydride [3]

Thermal stability of TiH$_2$ - HV

- Microhardness measurement of electrochemically loaded sample (20 mA, 239 h) compared with results for pure Ti (as received) – isochronally annealed 50°C/50 min

- Oxygen diffusion into Ti matrix
- Thermal stabilization of dislocations by H
- Homogenization of H distribution
- Different behavior for loaded and opposite side

Hydrogen stabilizes dislocations at higher temperatures (T > 300°C).
Thermal stability of TiH$_2$ – DSC, thermogravimetry

$\alpha \rightarrow \beta$-Ti transformation at $\approx 880^\circ$C

- hydrogen release from defects
  - minor mass change at $\approx 520^\circ$C – $550^\circ$C
- vacancy clusters, dislocations, grain boundaries – different binding energies
- decomposition of TiH$_2$ ($\delta \rightarrow \beta$)
  - major mass change at $\approx 620^\circ$C
Our view on different structure of gas- and electrochemically loaded samples was confirmed by XRD.

Phase transformation $\alpha$-Ti $\rightarrow$ $\delta$-TiH$_2$ introduces **dislocations** into the sample. 
$\rightarrow$ microhardness enhancement 
$\rightarrow$ dislocations stable at higher temperatures due to bonded hydrogen 
$\rightarrow$ embrittlement (cracks) due to reduced mobility of dislocations

Absorbed hydrogen present in form of $\delta$-TiH$_2$ and **bonded to defects** of different bonding energies (**vacancy clusters**, dislocations, grain boundaries).

H-induced vacancy clusters are **formed** at lower temperature or large loading current, when the vacancy diffusion is slow enough for cluster agglomeration. At higher temperatures or for small loading current vacancies diffuse to sinks at dislocations and grain boundaries and vacancy clusters are **not formed**.

Mean vacancy **cluster size** depends on loading conditions and bonded H.