In situ studies of hydrogen desorption from metallic hydrides by neutron diffraction

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Outline

✓ Short introduction to metallic hydrides (MH)
✓ Neutron diffraction for MH investigation
  o Steady state structural analysis
  o Out of equilibrium study by coupled TDS/ND
✓ The peculiar cases of TiNiH$_x$ and YFe$_2$H$_x$
✓ Conclusions
Short introduction to metallic hydrides

Metallic hydride for solid gas storage

▷ Solid gas route (P_{eq}, C(x), T)

\[ M + \frac{x}{2} H_2 \leftrightarrow MH_x \]
Short introduction to metallic hydrides

Metallic hydride for electrochemical storage

Electrochemical route (\(E_{eq}, Q(x), T\))

\[
M + x H_2O + x e^- \leftrightarrow MH_x + xOH^-
\]

\[
E_{eq}^{MH_x} = -\frac{RT}{nF} \ln P_{H_2} - 0.926 \quad \text{[in V vs Hg/HgO]}
\]

Non aqueous electrochemical route

\[
MH_x + x Li^+ + x e^- \leftrightarrow M + x LiH
\]

Some successful applications of hydrides...

HEV Toyota Prius

NiMH traction batteries for Nice trams

Other applications - emergency light units, telecommunications, cordless vacuum...

Introduction Neutrons for MH Case of TiNiHₓ Case of YFe₂Hₓ Conclusions
Neutron diffraction for MH investigation

✓ Crystal structure determination
  - Quantification and location of H(D) content
  - Evidence of phase transitions as a function of H(D) content

   Example: In-situ ND of LaNi$_5$-type electrodes

✓ Practical advantages of using ND as diffraction tool:
  - Bulk analysis (high penetration depth of neutrons)
  - Adaptable sample environment (furnace, cryostat, electrochemical cell...)
  - Adapted time resolution for thermal desorption

Latroche et al. JALCOM 293-295 (1999) 673
Thermal desorption spectroscopy (TDS)

Gas release measurement ($H_2$) while heating in a low pressure atmosphere

Potential energy diagrams

Heating ramp

$T$ (K) vs. $t$ (s)

TDS Spectrum

$dn/dt$ ($\alpha$, $P$) vs. $T$ (K)
Thermal desorption spectroscopy (TDS)

- **TDS: Experimental method**

\[ \frac{dn}{dt} = \frac{V}{K T} \frac{dP}{dt} + \frac{S}{K T} P \]

- Variation of P in the chamber
- Removal of gas by pumping

**Case of TiNiH\textsubscript{x}**

**Case of YFe\textsubscript{2}H\textsubscript{x}**

**Conclusions**
Thermal desorption spectroscopy (TDS)

- TDS: Experimental method

\[
\frac{dn}{dt} = \frac{V}{K} \frac{dP}{dt} + \frac{S}{K} P
\]

Variation of \( P \) in the chamber  
Removal of gas by pumping

Small volume (\( V \))  
High pumping rate (\( S \))

\[
\frac{dn}{dt} \propto P
\]

Case of TiNi\(_x\)H\(_x\)  
Case of YFe\(_2\)H\(_x\)  
Conclusions
TDS: what information can be obtained?

- Temperature assessment of discrete desorption “states” (TDS peaks)
- Populations (integrated areas) and related activation energies (Kissinger plots)
- Determination of rate limiting steps (surface, trapping, diffusion, phase transformation) with a valid kinetic model: full spectra description.

Example: TDS from PdHₓ

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TDS vs. ND

**TDS**
- Amount of desorbed $H_2$
- Desorption mechanism
  - Surface recombination
  - $H$ - Diffusion
  - Phase transformation

**ND**
- Amount and location of $H$ in bulk
- Crystal structure
  - Phase transformation vs $H$-content
  - Order-disorder transitions
  - Amorphisation
Combined measurements TDS – ND

Silica container  Vacuum and T connections  Neutron beam line ILL – D1B

- Thermocouple
- Furnace
- MH sample
- 400 Detectors
- Neutron beam

Introduction  Neutrons for MH  Case of TiNiH\textsubscript{x}  Case of YFe\textsubscript{2}H\textsubscript{x}  Conclusions
The case of TiNi-H$_2$
Sorption properties of the TiNi-H$_2$ system

Absorption by solid gas reaction: $T = 150^\circ$C, $P_{D_2} = 4$ MPa, $t = 2$ weeks

Measured concentration: TiNiD$_{1.35}$

$Pm$ $3m$

$\text{Vol/TiNi} = 27$ Å$^3$

*Case of TiNiH$_x$*

*Case of YFe$_2$H$_x$*

*Conclusions*

Structural properties of the α phase

\[ Pm\text{~}\overline{3}m \quad D/\text{TiNi} = 0.29 \]
\[ \text{Vol}/\text{TiNi} = 28.7 \text{ Å}^3 \]

3.057 Å

Conclusions
Structural properties of the B phase

$D/TiNi = 1.14$

$H(D)$

$Ni$

$Ti$

Soubeyroux et al., JALCOM 196 (1993) 127
Hydrogen desorption from TiNiH$_{1.4}$

One-step desorption

$\beta \rightarrow \alpha$ transformation

Three-step desorption

Introduction

Case of TiNiH$_x$

Case of YFe$_2$H$_x$

Conclusions
Coupled TDS-ND experiment

Introduction

Case of TiNiH_x

Case of YFe_2H_x

Conclusions
E-TiNiH_{1.4}

Case of TiNiH_{x}

Introduction

Neutrons for MH

Case of TiNiH_{x}

Case of YFe_{2}H_{x}

Conclusions
Results of Rietveld refinement

Phase content (wt%) vs. T (K)

- α phase
- β phase
- γ phase

Introduction
Case of TiNiH
Case of YFe2H
Conclusions
\[ I4/mmm \]
\[
\begin{align*}
D/TiNi &= 1.14 \\
Vol/TiNi &= 30.1 \, \text{Å}^3
\end{align*}
\]

\[ P4/mmm \]
\[
\begin{align*}
D/TiNi &= 0.7 \\
Vol/TiNi &= 29.4 \, \text{Å}^3
\end{align*}
\]

\[ Pm\overline{3}m \]
\[
\begin{align*}
D/TiNi &= 0.29 \\
Vol/TiNi &= 28.7 \, \text{Å}^3
\end{align*}
\]
Comparison of ND and TDS H-contents

Deuterium content (D/TiNi)

- TDS (spectrum integration)
- ND (ΣD-occupancies)

Introduction
Case of TiNiHx
Case of YFe2Hx
Conclusions
Comparison of ND, TDS and DSC

DSC

Heat Flow (W/g)

Desorption $H_2$

Crystallisation

TDS

T(K)

P (bar)

ND

Neutrons for MH

Introduction

Case of TiNiH$_x$

Case of YFe$_2$H$_x$

Conclusions
The case of $\text{YFe}_2\text{-H}_2$
**Motivation**

Multi-peak TDS spectra of Laves C15 hydrides attributed to H-desorption from energetically different interstitial sites

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**Stern et al. JALCOM 88 (1982) 431**

**Park et al. Scr. Metall. 23 (1989) 1525**

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**Introduction**

- Neutrons for MH
- Case of TiNiHₓ
- Case of YFe₂Hₓ

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**Conclusions**
Coupled TDS-ND experiment for YFe$_2$D$_{4.2}$
Coupled TDS-ND experiment for YFe$_2$D$_{4.2}$

Phase transformations

Order-disorder transitions

C15

380K  monoclinic
Thermodynamic & crystal structure for YFe$_2$-D$_2$

- Multi-plateau isotherms

![Graph showing multi-plateau isotherms with various phases and structural changes.]

V. Paul-Boncour, JSSC 142 (1999) 120

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Introduction $\rightarrow$ Neutrons for MH $\rightarrow$ Case of TiNiH$_x$ $\rightarrow$ Case of YFe$_2$H$_x$ $\rightarrow$ Conclusions
**Simulation of the TDS spectrum**

Successive phase transformation: Johnson-Mehl-Avrami (JMA) equation

\[ F_i = 1 - \exp\left\{-\left(k_i t\right)^{n_i}\right\}, \quad k_i = k_o \exp\left(-\frac{E_i}{RT}\right), \quad K_o \sim h T/K \sim 10^{-13} \text{s}^{-1} \]

\[ F_i \approx 1 - \exp\left\{-\left(k_i \frac{RT^2}{\beta E_i}\right)^{n_i}\right\} \]

\[ \frac{dF_i}{dt} = \eta_i k_i (1 - F_i) \left[- \ln(1 - F_i)\right]^{(n_i - 1)/n_i} \]

\[ \Rightarrow \text{Fit of TDS spectrum to i-phase transformations} \]

\[- \frac{dx}{dt} = \sum_{i=1}^{n} \Delta x_i \frac{dF_i}{dt} \]

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**Introduction**

**Neutrons for MH**

**Case of TiNiHₓ**

**Case of YFe₂Hₓ**

**Conclusions**
Fit of the TDS spectrum

<table>
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<tr>
<th>Peak</th>
<th>$E_a$ (kJ/mol)</th>
<th>$n$</th>
<th>$\Delta x$ (D/f.u.)</th>
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</table>
Comparison of ND and TDS H-contents

![Graph showing comparison of ND and TDS H-contents](image)

- $x_{PD}$ (ΣD-occupancies)
- $x_{TDS}$ (spectrum integration)
- C15-Volume

T. Leblond et al., IJHE, 34(2009) 2278
Conclusions (I)

✓ Thermal desorption from TiNiD$_{1.4}$ hydride occurs through an intermediated hydride phase of medium H-content: $\gamma$-TiNiD$_{0.7}$.

✓ $\gamma \rightarrow \alpha$ phase transformation generates compound amorphisation.

✓ DSC measurements are explained by the combined effects of endothermic hydrogen desorption and exothermic alloy crystallization.
Conclusions (II)

✓ Multi-peak TDS spectrum for YFe$_2$ hydride is well-described by consecutive phase transformations.

✓ Multiple C15 Laves phases have been evidenced by ND and XRD diffraction measurements.

✓ Same description may account for multi-peak TDS spectra observed for many C15 Laves phases.
Conclusions (III)

✓ TDS set-up can be easily implemented in ND beam-line

✓ Coupling of TDS - ND techniques is a very powerful tool to characterize hydrogen desorption from solids, particularly when phase transformations take place
Acknowledgments

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