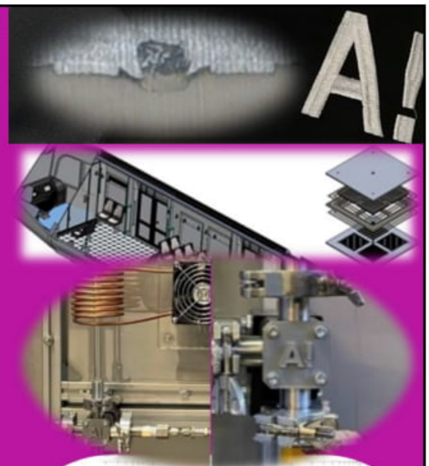
Department of Energy and Mechanical Engineering (EME)



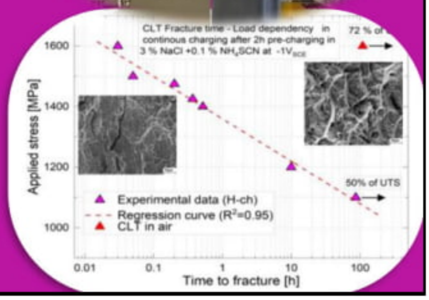
Hydrogen Breakfast Series #5

Standardization & Material challenges in hydrogen transportation & storage

Pedro Vilaça
Head of Department of EME
Professor on joining of materials and non-destructive testing

Aalto University
School of Engineering

Aalto, 9th April 2025



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Agenda (1/3)

- **Introduction**
  - **Historical perspective** on the contribution by M2P research group of **EME department of Aalto**, to research in hydrogen technology and economy
  - Overview of **Aalto infrastructure** dedicated for research of hydrogen interaction with engineering materials (with focus on distinct “home-made” equipment)
  - Fundaments on the **Hydrogen interaction with steels** and inherent **Hydrogen embrittlement (HE)** effect on their mechanical strength

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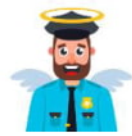
Agenda (2/3)

- ☞ **Hydrogen embrittlement effect on the mechanical strength of steels**
  - Evaluation of modern martensitic high-strength steels
  - Artificial neural network-based prediction
  - Overview of ongoing Aalto's research on NER/H2SIPP
- ☞ **Hydrogen-as-a-probe for high-resolution testing of steels**
  - Introduction to concept
  - Overview of background research for enhanced reliability
  - Application to an ex-service steel component from power plant

hydrogen
Bad Cop



hydrogen
Good Cop

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Agenda (3/3)

- ☞ **Aalto's innovation in manufacturing of Fuel Cells / Eletrolyzers**
  - Introduction to the **enabler new manufacturing** solutions by EME of Aalto
  - New concept of **Multi-Cell Panel** (MCP-FC/E) allowing structural integration

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Introduction (1/3)

Historical perspective on contribution by Materials and Manufacturing to Products (M2P) research group of Aalto/ENG/EME to research in hydrogen technology

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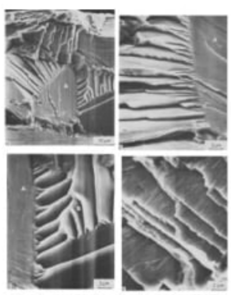
Historical perspective

The origins of research on H-metal interaction at Aalto



H.Hänninen, T.Hakkarainen (1979)
Fractographic characteristics of a hydrogen-charged AISI 316 type austenitic stainless steel. Metallurgical Transactions A. doi: 10.1007/BF02811667

Influence of Nitrogen Alloying on Hydrogen Embrittlement in AISI 304-Type Stainless Steels

SIMO-PEKKA HANNULA, HANNU HÄNNINEN, and SEPPO TÄHTINEN

SIMO-PEKKA HANNULA, formerly with Helsinki University of Technology, Laboratory of Physical Metallurgy, SF-02150 Espoo 15, Finland, is now a Research Fellow with the Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853. HANNU HÄNNINEN and SEPPO TÄHTINEN are Research Officers, Technical Research Centre of Finland, Metals Laboratory, Metallimiehenkuja 6, SF-02150 Espoo, Finland.
Manuscript submitted November 1, 1983.

METALLURGICAL TRANSACTIONS A

Aspects of the intertwined long-history of Aalto + VTT cooperation

***In Situ* Observations on Effects of Hydrogen on Deformation and Fracture of A533B Pressure Vessel Steel**

H.E. Hänninen, T.C. Lee, I.M. Robertson, and H.K. Birnbaum

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Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

Nuclear programme (FINNUS) supported by STUK and VTT

Study of H-metal interaction, local ordering, and defects in nuclear materials using hydrogen-as-a-probe for mechanical spectroscopy technique [1-4]

1990 — 2005


International Journal of Pressure Vessels and Piping

Overview of the nuclear power plant structural integrity research in Finland

Mechanical Spectroscopy Apparatus:

- Study of transitions corresponding to atomic or molecular motions
- High-sensitivity to the state of the lattice defects in crystals
- Measurement temperature range from 100 K to 1000 K

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Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

EU project (Charge & load)

Hydrogen embrittlement and delayed fracture of advanced multiphase high-strength steels [5]

2005 — 2015

Thermal Desorption Spectroscopy (TDS 1) apparatus:

- High-sensitivity study of hydrogen uptake and trapping in steels and alloys
- Detection of the hydrogen trapping sites in materials
- Measurement temperature range from RT to 1500 K

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Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

EU project (Charge & load)

EU project (HYDRAMICROS)

Hydrogen sensitivity of different advanced high-strength microstructures [9-11]

2005 — 2015

RFCS project (Coal and Steel)

Interaction of hydrogen with austenitic stainless steels and pure nickel. Development of advanced computational modeling of hydrogen solubility and diffusion [6-8]

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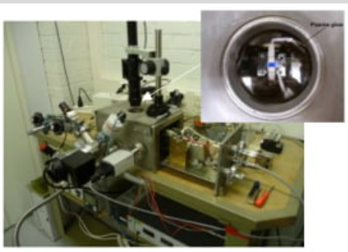
Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

Nuclear materials and radiochemistry doctoral programme (YTERA)

Hydrogen sensitivity of reduced activation oxide dispersion strengthened (ODS) high-strength steels [12-16]

2010 — 2015



Hydrogen Charging Process Instrument:

- Hydrogen charging at elevated temperatures
- In-situ mechanical testing
- In-situ optical monitoring

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Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

Method of **quantitative hydrogen sensitivity assessment** in business application [23-25]

BF R2B project (QUCAM)

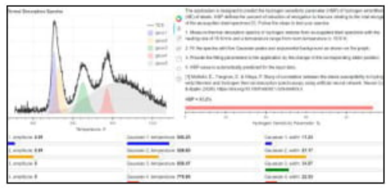
AI based software for quantitative analysis of hydrogen sensitivity of steels:

- TDS data processing
- Startup launched in 2020 (Metmod Oy)

2015 — 2020

Thermal Desorption Spectroscopy (TDS 2) apparatus:

- Automatic specimen loading
- Measurement temperature range from RT to 1100 K



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Historical perspective

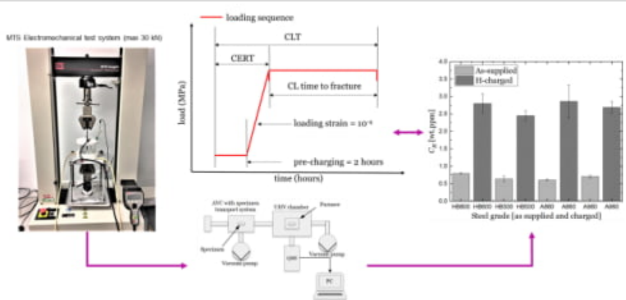
Research on Hydrogen-to-metal interaction at Aalto

ISA AALTO HydroSafeSteels,
Evaluation of the effects of hydrogen on the mechanical performance of modern ultra high-strength steels (UHSS) for demanding applications

BF project (ISA)

2019 — 2021

Hydrogen sensitivity of UHSS



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Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

New design for the PEM Fuel Cells and Eletrolyzers based on Aalto's invented advanced solution for joining metal-to-polymer: Through Slot Extrusion Joining

BF R2B
(THEW→TSEJ)

2020 — 2021

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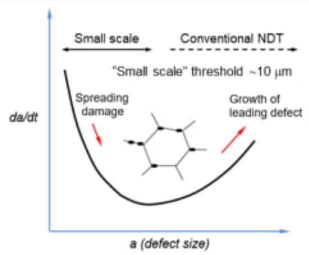
Historical perspective

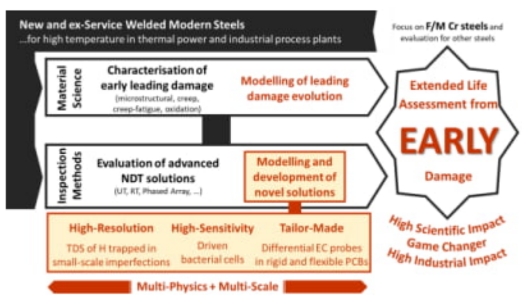
Research on Hydrogen-to-metal interaction at Aalto

Aalto is pioneer in **using hydrogen-as-a-probe** to develop new Non-Destructive Testing (NDT): TDS of **hydrogen** trapped from the atomic to grain-scale imperfections provides high-resolution assessment of early small-scale damage in energy structural systems; **Hydrogen-probe analysis of creep/creep-fatigue defects in steels at early stage**

RCF project
(EARLY)

2020 — 2023





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Historical perspective

Research on Hydrogen-to-metal interaction at Aalto

Hydrogen Safety and Improved Permit Processes (H2SIPP):
To develop strategies to delimit key barriers identified in recent work for the implementation of hydrogen in the Nordic countries:

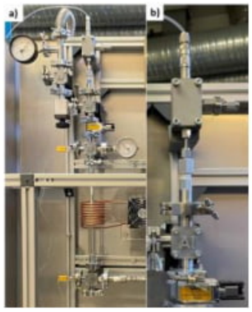
- Permit processes and social acceptance
- Knowledge transference to society and stakeholders with risk analysis
- Key-safety features: Materials safety + Safety distances

NER project (H2SIPP)

2023 — 2026

New **Thermal H-Charging** equipment:

- Physisorption only
- Reliable ⇔ repeatable H-charging
- H-safe operation
- Low cost



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Aalto Dec 2024

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Historical perspective

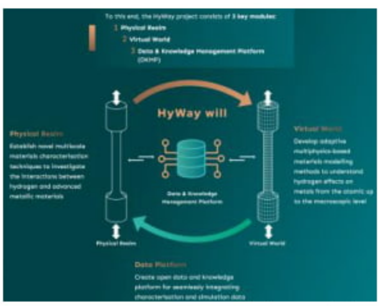
Research on Hydrogen-to-metal interaction at Aalto

Interaction of hydrogen with OFP copper and cast iron used for nuclear waste disposal [17-22]

Finnish Research Programme on Nuclear Waste Management (KYT)

to be continued…

2024 — 2027



https://hywayproject.eu/

Multiscale characterization and simulation for Hydrogen Embrittlement Assessment:
To develop highly flexible and efficient modelling and characterization suites for revealing interactions between hydrogen and advanced materials under service conditions of the hydrogen storage and transport infrastructure

EU HORIZON (HyWay)

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Historical perspective

Supporting list of references (1/3)

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2. Hydrogen-probe mechanical spectroscopy for studying local ordering in concentrated substitutional alloy, Journal of Alloys and Compounds 310, 200–204, 2000.
3. A new method for studying thermal desorption of hydrogen from metals based on internal friction technique, Physica Scripta: Topical Issues, T94, 111-120, 2001.
4. Interactions of hydrogen in copper studied by internal friction technique, Material Science and Engineering A 370, 218–221, 2004.
5. Hydrogen embrittlement and delayed fracture of advanced multiphase high-strength steels, Luxemburg / Publications Office of the European Union (2013) [Report].
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8. Hydrogen solubility and diffusion in austenitic stainless steels studied with thermal desorption spectroscopy, steel research int. 82, No. 13, 2010.

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Historical perspective

Supporting list of references (2/3)

9. Role of Nonmetallic Inclusions in Hydrogen Embrittlement of High-Strength Carbon Steels with Different Microalloying, The Minerals, Metals & Materials Society and ASM International, doi: 10.1007/s11661-014-2447-2, 2014.
10. Hydrogen effects on fracture of high-strength steels with different micro-alloying, Corrosion Review, doi 10.1515/corrrev-2015-0044, 2015.
11. Hydrogen sensitivity of different advanced high strength microstructures (HYDRAMICROS), final report, doi 10.2777/07315, ISBN 978-92-79-45820-0, 2015.
12. Comparative study of hydrogen uptake and diffusion in ODS steels, Fusion Engineering and Design 88, 2607– 2610, 2013.
13. Hydrogen effects on tensile properties of EUROFER 97 and ODS-EUROFER steels, Journal of Nuclear Materials 444, 435–440, 2014.
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15. Hydrogen-induced crack nucleation in tensile testing of EUROFER 97 and ODS-EUROFER steels at elevated temperature, Journal of Nuclear Materials 466, 286-291, 2015.
16. Investigation of microstructure changes in ODS-EUROFER after hydrogen loading, Journal of Nuclear Materials 468, 355-359, 2016.

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Historical perspective

Supporting list of references (3/3)

17. Hydrogen-enhanced creep and cracking of oxygen-free phosphorus-doped copper, Scripta Materialia 67, 931–934, 2012.
18. Hydrogen-Induced Mechanical Losses in Oxygen-Free Copper, Solid State Phenomena 184, 122-127, 2012.
19. Effects of hydrogen and impurities on void nucleation in copper: simulation point of view, Philosophical Magazine, doi: 10.1080/14786435.2014.962642, 2014.
20. Hydrogen effects on mechanical performance of nodular cast iron. Corrosion Reviews, 37(5), 441-454. doi: 10.1515/corrrev-2019-0007, 2019.
21. Hydrogen embrittlement of nodular cast iron, Materials and Corrosion, doi : 10.1002/maco.202011682, 2020.
22. Sulphide-induced stress corrosion cracking and hydrogen absorption of copper in deoxygenated water at 90°C, Materials and Corrosion, doi : 10.1002/maco.202011695, 2020.
23. Study of correlation between the steels susceptibility to hydrogen embrittlement and hydrogen thermal desorption spectroscopy using artificial neural network, Neural Computing and Applications, 32:14995–15006, 2020.
24. Improved Accuracy of Thermal Desorption Spectroscopy by Specimen Cooling during Measurement of Hydrogen Concentration in a High-Strength Steel, MDPI, 2020.
25. Resolution adopted by the General Assembly on 25 September 2015, Transforming our world: the 2030 Agenda for Sustainable Development

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Recent publications by Vilaca's team

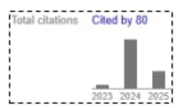
1. M.I.Silva, S.Khakalo, A.Agarwal, R.Pohja, P.Vilaça (2025) **Application of hydrogen-as-a-probe to inspect the metallurgical condition and imperfections of a 13CrMo4-5 ex-service steam header component from power plant.** Ready to be submitted for publication
2. M.I.Silva, P.Auerkari, R.Pohja, T.Andersson, P.Vilaça (2025) **On the Ac1 and Ac3 transformation temperatures of 1Cr-0.5 steels.** Submitted
3. M.I.Silva, G.Sorger, E.Malitckii, P.Vilaça (2024) **Hydrogen-as-a-probe applied to investigate the influence of extraction and preparation methods on TDS spectra of 13CrMo4-5 samples.** Journal of Materials Science: Metals and Corrosion. doi: 10.1007/s10853-024-10383-3
4. M.I.Silva , E.Malitckii , P.Lehto , P.Vilaça (2024) **Influence of sample extraction location on thermal desorption spectroscopy from a heat-resistant 13CrMo4-5 steel plate and correlation with microstructure features.** Materialia . doi: 10.1016/j.mtla.2024.102130
5. R.Pohja, S.B.Holmström, S.Khakalo, P.Auerkari, P.Vilaça (2024) **Evolution and criteria for early creep damage. Materials at High Temperatures.** doi: 10.1080/09603409.2023.2295599
6. M.I.Silva, E.Malitckii, T.G.Santos, P.Vilaça (2023) **Review of conventional and advanced non-destructive testing techniques for detection and characterization of small-scale defects.** Progress in Materials Science. doi: 10.1016/j.pmatsci.2023.101155

↳ **594 refs, over 69 pages**

33.6
Impact Factor

59.6
CiteScore

ASJC Category	Quartile	Percentile	Rank
General Materials Science	Q1	99th	4 / 463



Aalto's publication reached in less than 2 years higher citation record than CiteScore of PMS journal

(citation counts in a range of 4 years)

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Recent publications by Vilaca's team

👉 **Eric Komla Fangnon:** recipient of 2024 ENG's Doctoral Thesis Award

7. E.Fangnon, E.Malitckii, R.Latypova, and P.Vilaça (2023) **Prediction of hydrogen concentration responsible for hydrogen-induced mechanical failure in martensitic high-strength steels.** Journal of Hydrogen Energy. doi:10.1016/j.ijhydene.2022.11.151
8. R.Pohja, P.Auerkari, P.Vilaça (2022) **Modelling for creep cavitation damage and life of three metallic materials".** Journal of Materials at High Temperatures. doi: 10.1080/09603409.2021.2024420
9. E.Fangnon, Y.Yagodzinskyy, E.Malitckii, S.Mehtonen, E.Virolainen, P.Vilaça (2021) **Determination of critical hydrogen concentration and its effect on mechanical performance of 2200 MPa and 600 HBW martensitic ultra-high-strength steel**. Metals. doi: 10.3390/met11060984
10. E.Malitckii, E.Fangnon, P.Vilaça (2020) **Evaluation of steels susceptibility to hydrogen embrittlement: A thermal desorption spectroscopy-based approach coupled with artificial neural network**. Materials. doi: 10.3390/ma13235500
11. E.Malitckii, E.Fangnon, P.Vilaça (2020) **Study of correlation between the steels susceptibility to hydrogen embrittlement and hydrogen thermal desorption spectroscopy using artificial neural network**. Neural Computing and Applications. doi: 10.1007/s00521-020-04853-3
12. E.Fangnon, E.Malitckii, Y.Yagodzinskyy, P.Vilaça (2020) **Improved accuracy of thermal desorption spectroscopy by specimen cooling during measurement of hydrogen concentration in a high-strength steel**. Materials. doi:10.3390/ma13051252
13. E.Malitckii, Y.Yagodzinskyy, P.Vilaça (2019) **Role of retained austenite in hydrogen trapping and hydrogen-assisted fatigue fracture of high-strength steels**. Materials Science and Engineering: A. doi: 10.1016/j.msea.2019.05.103

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Introduction (2/3)

Overview of Aalto infrastructure dedicated for research of hydrogen interaction with engineering materials

- **Focus on distinct "home-made" equipment**

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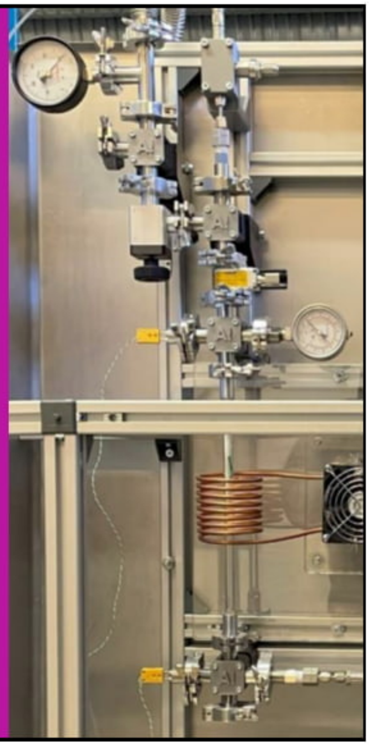

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Aalto's research infrastructure

H interaction with metals: Typical research flow methods

Hydrogen charging
(including with *in-situ* mech testing)

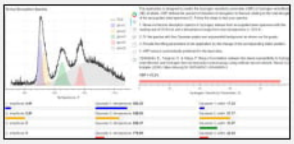
- **Electrochemical charging**
- Plasma charging
- **Thermal charging**

Hydrogen measurement

- **Thermal Desorption Spectroscopy (TDS)**
- Mechanical spectroscopy

Characterization

- **Analytical analysis and FEM modeling**
- **AI-based analysis**



+ Mechanical testing

- **CERT** (C^{te} Ext. Rate Test)
- **CLT** (C^{te} Load Test)
- **Fracture/Fatigue**
- **Charpy Impact**

+ Microstructural evaluation

- **SEM-EBSD-EDS**
- **Nano-tribointender**
- **Differential Scanning Calorimeter (DSC)**

Note:

- **Uniaxial CERT** (classic strength testing criteria ⇔ yields early-localized strain phenomena)
- **Uniaxial CLT** (quasi-creep damage phenomena ⇔ assessment of long-term safety)

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Introduction (3/3)

Fundaments on:

- **H-metal interaction**
- **Hydrogen embrittlement (HE) effect on mechanical strength of steels**

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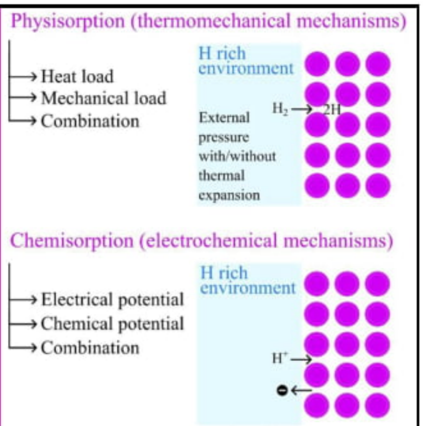

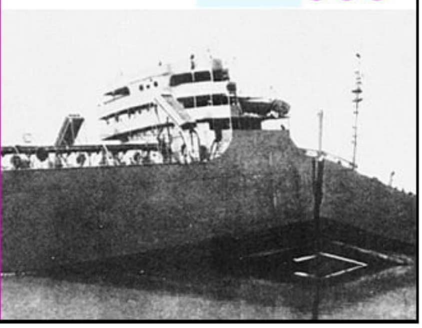

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H interaction with steels

Introduction to fundaments

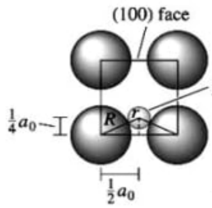
Some Facts:

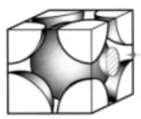
Lattice parameters in IRON:

- **BCC (α-iron):**
  - Radius iron atom, R_{BCC} = 0.1241 nm
  - Lattice size $a_0 \approx$ 0.2866 nm
  - $r_{intersticial}$ = 0.0361 nm

Hydrogen atom **radius** is:

- R_{H_atom} = **0.053 nm** (~Bohr radius)
- R_{C_atom} = 0.077 nm

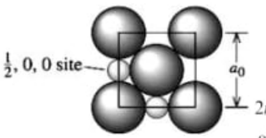




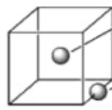
$$\left(\frac{1}{2}a_0\right)^2 + \left(\frac{1}{4}a_0\right)^2 = (r_{\text{interstitial}} + R_{\text{BCC}})^2$$

$$r_{\text{interstitial}} = \sqrt{0.02567} - 0.1241 = 0.0361 \text{ nm}$$

- **FCC (γ-iron):**
  - Radius iron atom, R_{FCC} = 0.1263 nm
  - Lattice size ≈ 0.3571 nm
  - $r_{intersticial}$ = 0.0522 nm



$$2r_{\text{interstitial}} + 2R_{\text{FCC}} = a_0$$



$$r_{\text{interstitial}} = \frac{0.3571 - (2)(0.1263)}{2} = 0.0522 \text{ nm}$$

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☞ ***…fewer atoms (e.g. C and H) are expected to stay at interstitial positions in BCC-iron than in FCC-iron***

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H interaction with steels

Introduction to fundaments: Typical hydrogen sources

Some Facts:

- **Manufacturing** of raw materials (e.g. metallurgical hydrogen content in a steel) and **fabrication** processes (e.g. welding)
- **Hydrogenated gas mixtures in active chemical environments** enhanced by electrical and/or mechanical energy (e.g. hydrogen sulfides H_2S -rich liquid flows in power plants)
- **Storage** (e.g. pressure vessels), **transport** (e.g. pipelines) and **operation** (e.g. components from combustion engines) of high-pressure and/or high-temperature hydrogen-rich gaseous environment
- **Cathodic protection** (e.g. in subsea pipelines)

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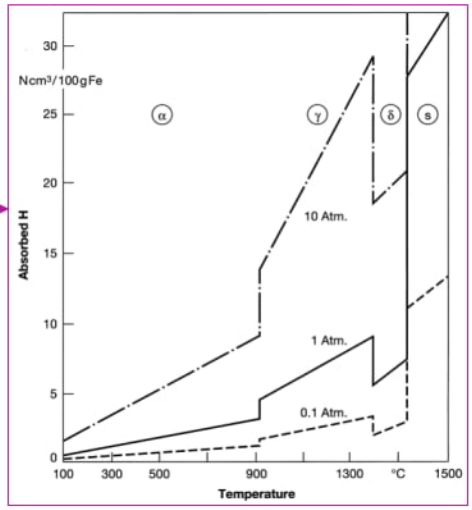
H interaction with steels

Introduction to fundaments

Some Facts:

- …If fewer atoms of **hydrogen** are expected to stay at interstitial positions in BCC (α-iron) than in FCC (γ-iron):
  - **Solubility of hydrogen**
    FCC (γ-iron) **>** BCC (α-iron)
  - **Dissolution energy for hydrogen**
    BCC (α-iron) **>** FCC (γ-iron)



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H interaction with steels

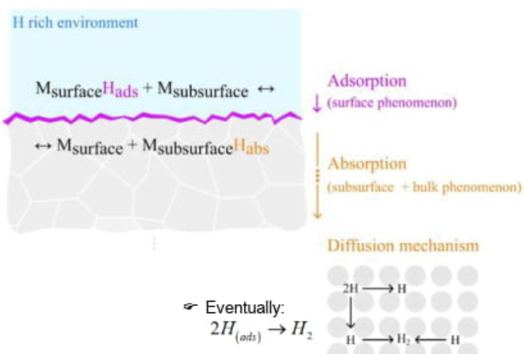
Introduction to fundaments: *H-charging (Adsorption + Absorption)*

Some Facts:

- Adsorption requires H_2 undergoes dissociation:

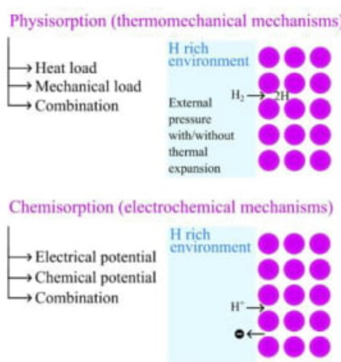
  $H_2 + 2M \leftrightarrow 2MH_{ads}$

- Only after **adsorption**, the **absorption** and/or **desorption** occurs:



- Eventually:
  $2H_{(ads)} \rightarrow H_2$

- **Adsorption** (gas-metal interaction) includes the mechanisms of **physisorption** and **chemisorption**:



- Electrolytic hydrogen system activates the Hydrogen Evolution Reactions (HER), e.g.:

  $H_2O + e^- + M \leftrightarrow OH^- + MH_{ads}$

  Hydroxyl ion (OH⁻)

in M.I.Silva et al. (2024) ***Hydrogen-as-a-probe applied to investigate the influence of extraction and preparation methods on TDS spectra of 13CrMo4-5 samples***. doi: 10.1007/s10853-024-10383-3

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H interaction with steels

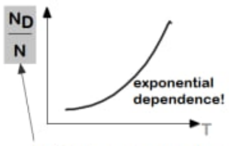
Introduction to fundaments: *H-diffusivity*

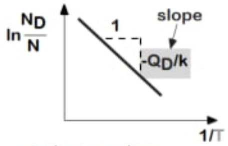
Some Facts:

- We can get Q from an experiment.
- Measure this...

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- Replot it...

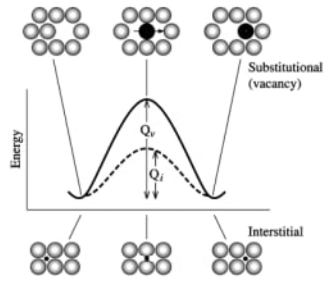




No. of defects; Activation energy

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

No. of potential defect sites. Temperature. Boltzmann's constant (1.38×10^{-23} J/atom K) (8.62×10^{-5} eV/atom K)



Schematic representation of the **DIFFUSION of an atom, interstitially and from its original position into vacant lattice site:**

- An activation energy Q_D has to be supplied to the atom so that it could break inter-atomic bonds and to move into new position

☹ At room temperature, the **diffusivity** of **hydrogen** in pure BCC (α-iron) is ~1x10^{-10} m^2/s, **ten order of magnitudes higher** than diffusivity of **carbon** and **nitrogen**, i.e. ~1x10^{-20} m^2/s

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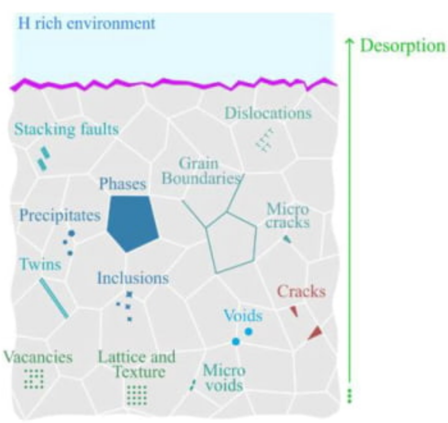
H interaction with steels

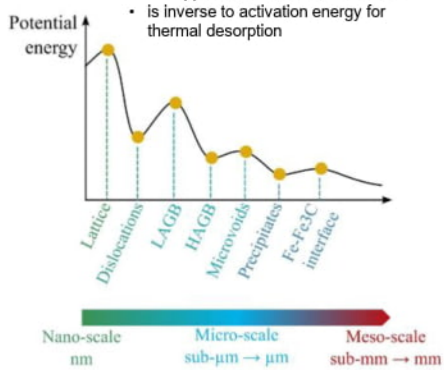
Introduction to fundaments: *H-trapping sites and their Energy of Activation*

Some Facts:



☞ **Potential energy**

- is inverse to the Gibbs free energy (G) and to the inherent stability of the H-trapped within the microstructure
- is inverse to activation energy for thermal desorption



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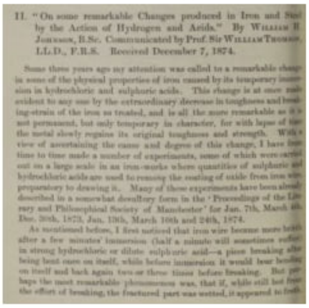
in M.I.Silva et al. (2024) **Hydrogen-as-a-probe applied to investigate the influence of extraction and preparation methods on TDS spectra of 13CrMo4-5 samples.** doi: 10.1007/s10853-024-10383-3

H embrittlement (HE) effect on steels

Introduction to fundaments: *Historical scope*

Some Facts:

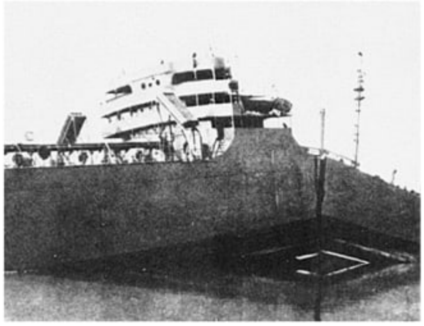
Working in the British steel industry at the **beginning of II Industrial Revolution**, the metallurgist **William Johnson** was the pioneer researcher investigating a mystery that affected the whole steel and wire drawing industry around **150 years ago** (doi: 10.1002/adem.202400776)


II. "On some remarkable Changes produced in Iron and Steel by the Action of Hydrogen and Acids." By WILLIAM H. JOHNSON, B.Sc. Communicated by Prof. Sir WILLIAM THOMSON, LL.D., F.R.S. Received December 7, 1874.

Some three years ago my attention was called to a remarkable change in some of the physical properties of iron caused by its temporary immersion in hydrochloric and sulphuric acids. This change is at once made evident to any one by the extraordinary decrease in toughness and breaking-strain of the iron so treated, and is all the more remarkable as it is not permanent, but only temporary in character, for with lapse of time the metal slowly regains its original toughness and strength. With a view of ascertaining the cause and degree of this change, I have from time to time made a number of experiments, some of which were carried out on a large scale in an iron-works where quantities of sulphuric and hydrochloric acids are used to remove the coating of oxide from iron wire preparatory to drawing it. Many of these experiments have been already described in a somewhat desultory form in the 'Proceedings of the Literary and Philosophical Society of Manchester' for Jan. 7th, March 4th, Dec. 30th, 1873, Jan. 13th, March 10th and 24th, 1874.

As mentioned before, I first noticed that iron wire became more brittle after a few minutes' immersion (half a minute will sometimes suffice) in strong hydrochloric or dilute sulphuric acid—a piece breaking after being bent once on itself, while before immersion it would bear bending on itself and back again two or three times before breaking. But perhaps the most remarkable phenomenon was, that if, while still hot from the effort of breaking, the fractured part was wetted, it appeared to

W. H. Johnson (**1875**) **On some remarkable changes produced in iron and steel by the action of hydrogen and acids**. Proc. Royal Society of London, 23, pp. 168-179.
Extract from https://royalsocietypublishing.org



During WWII, 12 USA ships, incl. 3 Liberty, broke in half without warning:

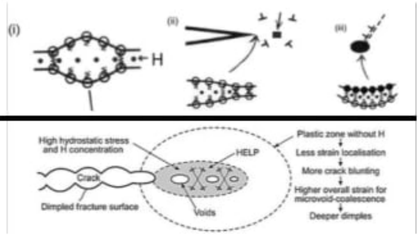
- **Cambridge Univ. demonstrated that fractures were due to low temperature embrittlement of steel. Welded hull construction, unlike riveted, allowed small cracks to propagate unimpeded**
- Crack nucleated at square corner of a hatch which coincided with a welded seam, both corner and weld acting as stress concentrators. A revolution in NDT technology immerged from this historic event

H embrittlement (HE) effect on steels

Introduction to fundaments: *Typical Damage Mechanisms*

Some Facts:

- **Hydrogen Enhanced Decohesion (HEDE)**
  - Embrittlement due to localized reduction in cohesive strength of the iron lattice hence assist the separation of cleavage planes or grain boundaries under a lower stress
- **Hydrogen Enhanced Localized Plasticity (HELP)**
  - Atomic hydrogen accelerate the dislocation mobility through an elastic shielding effect that cause a local reduction in shear stress. Local high strains due to hydrogen clusters around dislocations, might disrupt interfaces and structures



Schematic representation of Hydrogen Assisted Cracking (HAC) via HEDE and HELP

in Lynch, Stan (2012) Hydrogen embrittlement phenomena and mechanisms. Corrosion Reviews. 30 (3-4). doi: 10.1515/corrrev-2012-0502

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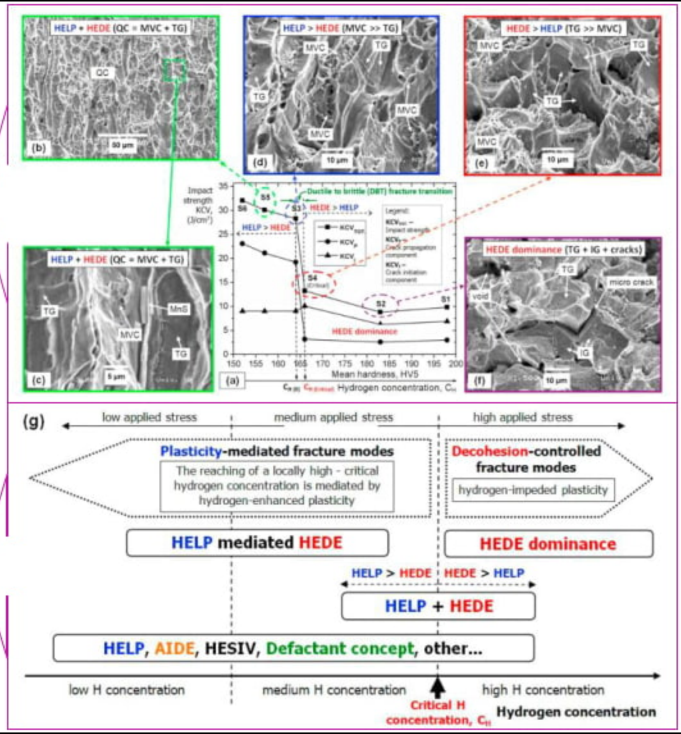
Xinfeng Li et al. (2024) **Review of the hydrogen embrittlement and interactions between hydrogen and microstructural interfaces in metallic alloys: Grain boundary, twin boundary, and nano-precipitate**. International Journal of Hydrogen Energy.
doi: 10.1016/j.ijhydene.2024.05.257

Fracture modes and mechanical properties drop, depending on hydrogen concentration and synergistically active HE mechanisms

*As proposed by Professor **Milos B. Djukic***
(University of Belgrade, Faculty of Mechanical Engineering, Serbia)

Unified HELP + HEDE model
synergy, and predominance of plasticity-mediated HE mechanisms and HEDE depending on hydrogen concentration



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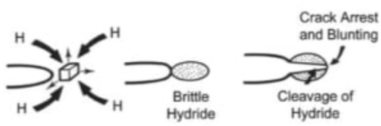
H embrittlement (HE) effect on steels

Introduction to fundaments: *Other Damage Mechanisms*

Some Facts:

- Hydrogen induced phase transformation (HIPT)



- Decohesive hydrogen fracture (DHF)
- Hydrogen assisted microvoid / nanovoid coalescence (HDMC / NVC)
- Hydrogen enhanced strain-induced vacancies (HESIV)
- Hydrogen assisted microfracture (changed: ductile to brittle fracture mode) (HAM)
- Mixed fracture (MF)
- Adsorption-induced dislocation emission (AIDE)
- Hydrogen enhanced macroscopic (ductility) plasticity (HEMP)

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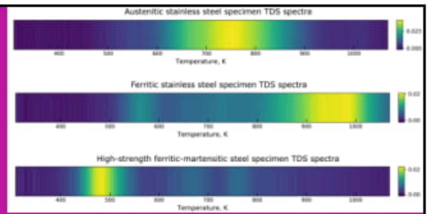
HE effect on the mechanical strength of steels (1/2)

- Evaluation of modern martensitic steels (UHSS)
- DANN-based prediction



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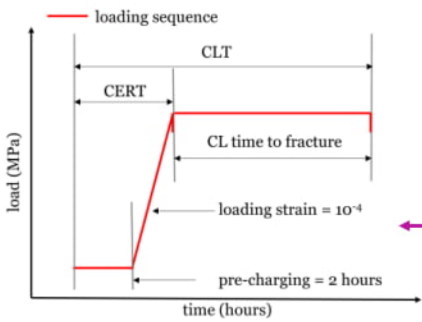
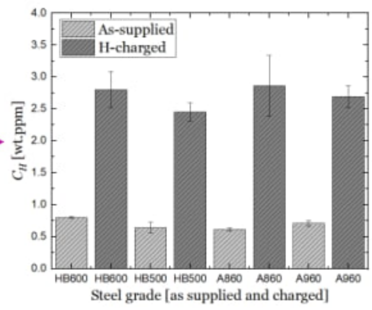
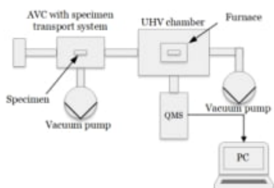
H embrittlement effect on steels

Aalto's typical research flow methods

MTS Electromechanical test system (max 30 kN)







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H embrittlement effect on steels

Hydrogen to Steel interaction: Evaluation of modern martensitic HSS

CERT performed under continuous hydrogen charging (+2h pre-charging) of MS-UHSS HB600

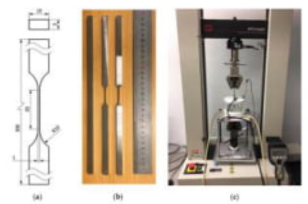

Figure 2. (a) Dimensions of mechanical testing (MT) specimens; (b) MT specimens prior to H-charging; (c) assembly of MT specimens with the electrochemical cell and loading unit for tensile testing (CERTs and CLTs) under continuous H-charging.

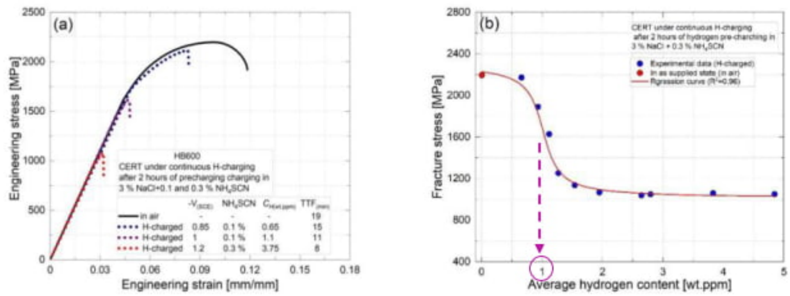

Figure 5. **(a)** Engineering stress versus strain curves of studied steel showing the effect of hydrogen on the tensile property of studied steel; **(b)** hydrogen embrittlement curve of tested steel showing a clear lower plateau at 1100 MPa.

in E. Fangnon, et al. (2021) **Determination of critical hydrogen concentration and its effect on mechanical performance of 2200 MPa and 600 HBW martensitic ultra-high-strength steel**. doi: 10.3390/met11060984

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H embrittlement effect on steels

Hydrogen to Steel interaction: Evaluation of modern martensitic HSS

Fractography from **CERT** under hydrogen charging (+2h pre-charging) of MS-UHSS HB600

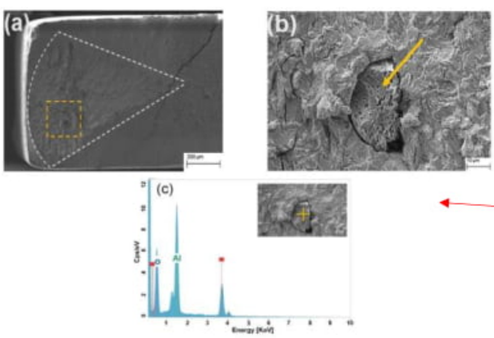

Figure 11. **(a)** Fractography of the specimen charged to 1.1 wt.ppm; **(b)** higher magnification of the yellow square in **(a)** showing the crack initiation from an inclusion, **(c)** revealed by energy dispersive spectroscopy (EDS) to be an Al_2O_3 particle.

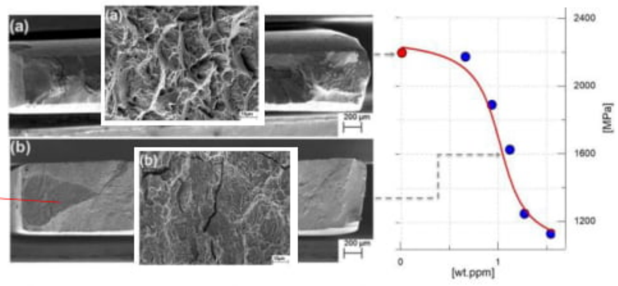

Figure 10. Fracture surface of the tensile specimens: **(a)** Tested in air without hydrogen charging; **(b)** electrochemical hydrogen charged to 1.1 wt.ppm.

in E. Fangnon, et al. (2021) **Determination of critical hydrogen concentration and its effect on mechanical performance of 2200 MPa and 600 HBW martensitic ultra-high-strength steel**. doi: 10.3390/met11060984

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H embrittlement effect on steels

Hydrogen to Steel interaction: Evaluation of modern martensitic HSS

CLT under hydrogen charging (+2h pre-charging) of MS-UHSS HB600

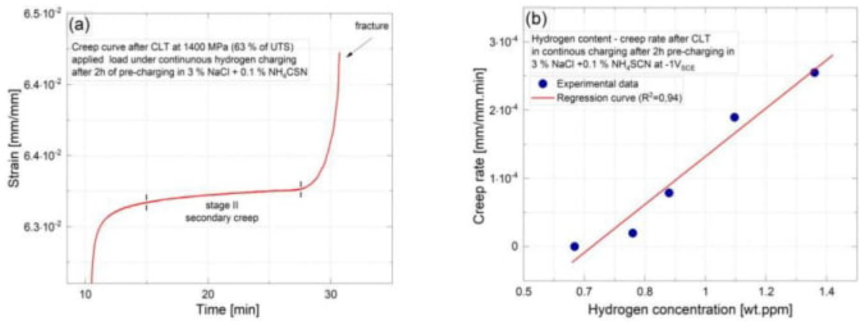

Figure 8. (**a**) Engineering strain versus time curve from CLT at 1400 MPa under continuous hydrogen charging; (**b**) creep rates as a function of hydrogen concentration.

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in E. Fangnon, et al. (2021) **Determination of critical hydrogen concentration and its effect on mechanical performance of 2200 MPa and 600 HBW martensitic ultra-high-strength steel**. doi: 10.3390/met11060984

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H embrittlement effect on steels

Hydrogen to Steel interaction: Evaluation of modern martensitic HSS

CLT under hydrogen charging (+2h pre-charging) of MS-UHSS HB600

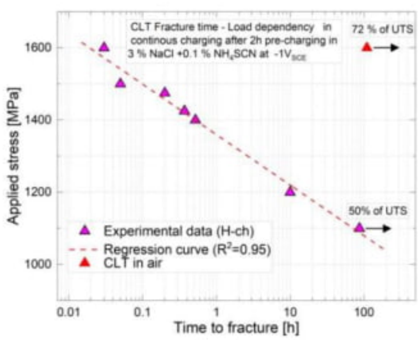

Figure 7. CLT-based results with applied load as a function of time to fracture. The CLT of hydrogen charged specimens are performed at continuous hydrogen charging, after 2 h of pre-charging under conditions corresponding to the critical hydrogen concentrations.

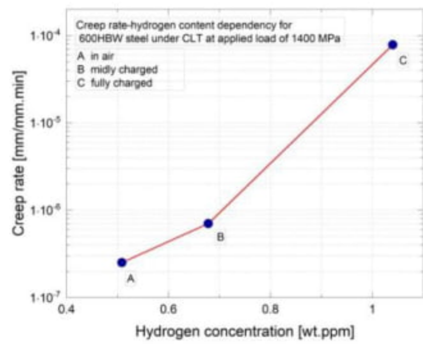

Figure 12. Creep rates in CLT under applied stress of 1400 MPa as a function of measured hydrogen concentration.

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in E. Fangnon, et al. (2021) **Determination of critical hydrogen concentration and its effect on mechanical performance of 2200 MPa and 600 HBW martensitic ultra-high-strength steel**. doi: 10.3390/met11060984

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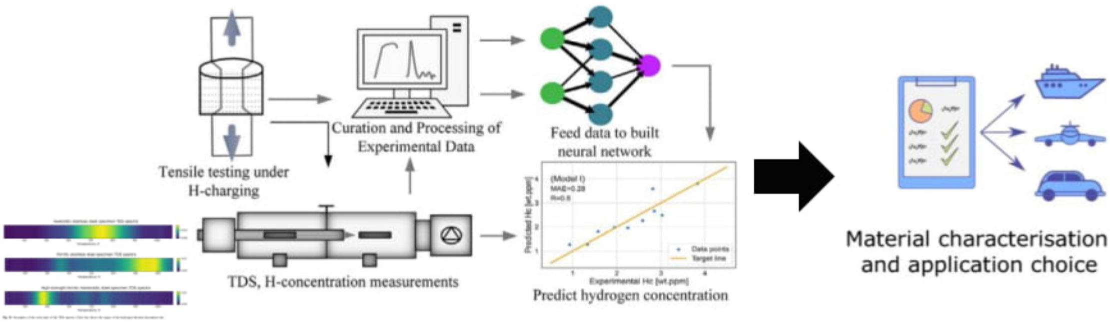
H embrittlement effect on steels

Deep Artificial Neural Network (DANN ⇔ Machine Learning)

Prediction of hydrogen content and material performance:

- **From** material characterization **To** fast material selection for H-rich environment



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in E. Fangnon et al. (2023) **Prediction of hydrogen concentration responsible for hydrogen-induced mechanical failure in martensitic high-strength steels**. doi:10.1016/j.ijhydene.2022.11.151

in E. Malitckii et al. (2020) **Evaluation of steels susceptibility to hydrogen embrittlement: A thermal desorption spectroscopy-based approach coupled with artificial neural network**. doi: 10.3390/ma13235500

H embrittlement effect on steels

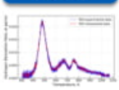
Deep Artificial Neural Network (DANN ⇔ Machine Learning)

Prediction of hydrogen content and material performance:

#	Steel	Elongation to fracture, (%)		HSP, (%)
		ε	ε_H	
1	AISI 304	83.7	32.9	60.7
2	AISI 409	33.5	11.3	66.2
3	AISI 441	29.1	7.7	73.3
4	VA1000_M05	6.2	0.84	86.4
5	VA1000_TM05	7.01	0.77	88.9
6	VA1200_MTM	8.3	0.78	90.5
7	VA1400_TM	5.4	0.34	93.7
8	HSS172600	3.4	0.13	96
9	HSS172601	4.8	0.17	96.4
10	VA1400_MTM	6.4	0.13	97.9

10 different steels

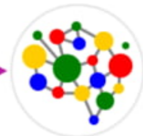
$\Delta\varepsilon$



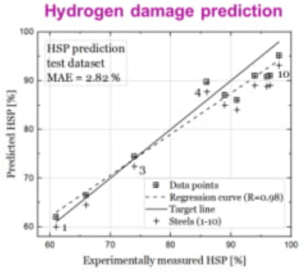
Training Data

Processed TDS

$$HSP = \frac{M_{P_{air}} - M_{P_H}}{M_{P_{air}}} * 100\%$$



Hydrogen damage prediction



Test Data 10 steels: Ferritic, austenitic, martensitic and dual phase

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in E. Malitckii et al. (2020) **Study of correlation between the steels susceptibility to hydrogen embrittlement and hydrogen thermal desorption spectroscopy using artificial neural network. Neural Computing and Applications**. doi: 10.1007/s00521-020-04853-3.

H embrittlement effect on steels

Deep Artificial Neural Network (DANN ⇔ Machine Learning)

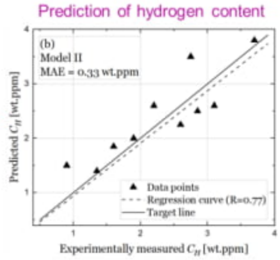
Prediction of hydrogen content and material performance:

Training Data

- Mechanical properties
- Mechanical properties (H-charged)
- Service conditions
- Hydrogen content
- $HSP = \frac{M_{p_{air}} - M_{p_H}}{M_{p_{air}}} * 100\%$

Test Data:
only mechanical properties
4 martensitic steels with different PAG morphologies

Prediction of hydrogen content

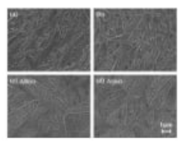


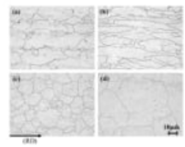
The developed DANN models can predict the HSP and C_{Hc} responsible for hydrogen damage of steels of different microstructural properties

HB500 + reheating at 860 °C = A860
HB500 + reheating at 960 °C = A960

lath-martensite and carbide morphology

Chemical composition [wt. %]	HB600	HB500
C	0.370	0.250
Mn	0.299	0.250
S	0.001	0.002
Al	0.430	0.095





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In E. Fangnon et al. (2023) **Prediction of hydrogen concentration responsible for hydrogen-induced mechanical failure in martensitic high-strength steels**. doi:10.1016/j.ijhydene.2022.11.151

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HE effect on the mechanical strength of steels (2/2)

- **Overview of ongoing Aalto's research on NER/H2SIPP**

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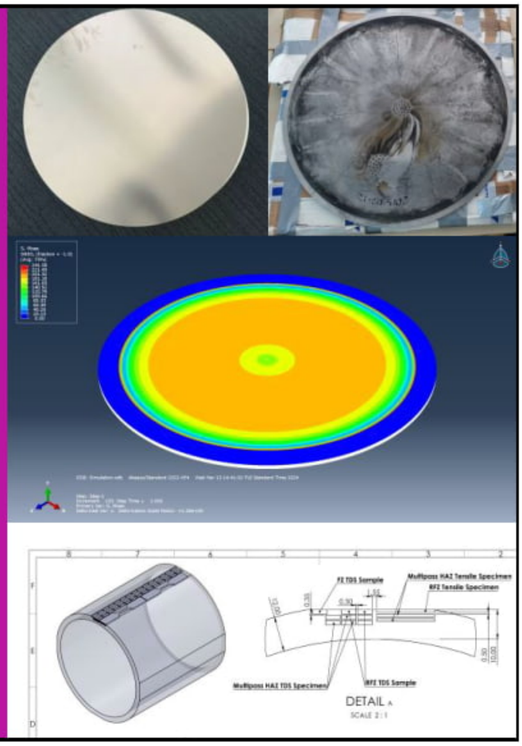

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H2S IPP Hydrogen Safety and Improved Permit Processes

NORDIC HYDROGEN VALLEYS

Pathways to 2030 and 2040

We will develop strategies to delimit key barriers identified in recent work for the implementation of hydrogen in the Nordic countries:

1) Permit processes and social acceptance
2) Knowledge transference to society and stakeholders with risk analysis
3) Key-safety features:
   - Materials safety
   - Safety distances

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Frontrunners within the hydrogen industry, local hydrogen energy systems, pipelines, refuelling stations, NGOs and public partners

H2S IPP

AFRY ÅF PÖYRY · NORDION ENERGI · hydri · GÄLLIVARE · BODENS KOMMUN · SSAB · SKOOGS Bränsle AB · GEN-H Hydrogen energy solutions · ENERGIGAS SVERIGE · ZELK

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A multidisciplinary and agile approach

H2S IPP

1. To suggest how to **improve permit processes**

Analyse law, permit processes and stakeholders. Work on **real cases, and comparing regions**

2. To present ways of working to increase the **social acceptance**

By theoretical and empirical frameworks and quantitative **risk analysis**

3a. To fill regulation gaps regarding **safety** calculations

Performing calculations and experiments on **material safety**

3b. To understand **hydrogen leakage from underground pipelines**

By calculations, experiments and development of theories for **safety distances**

4. Increase **stakeholder interaction** between disciplines, and countries etc.

By delivering research-based knowledge exchange and **communication**

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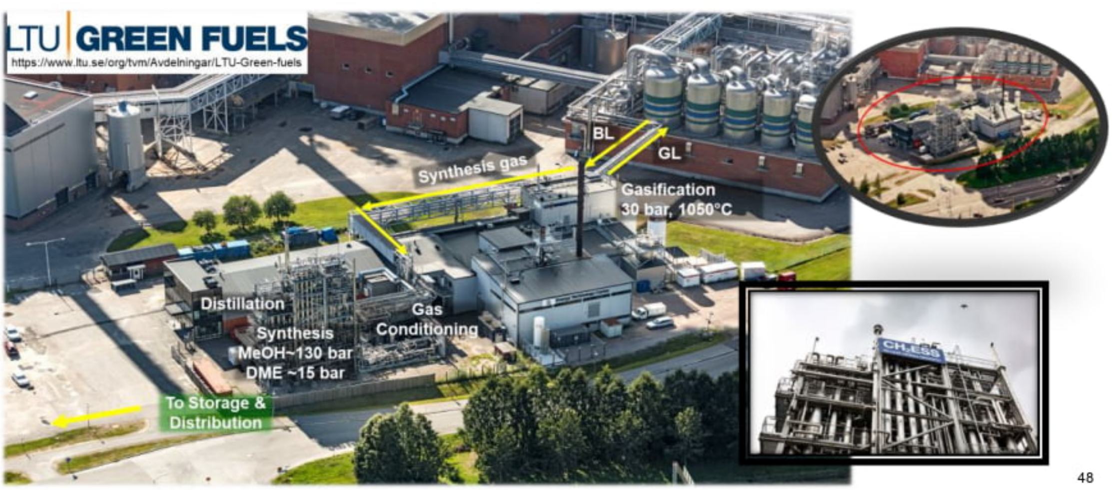
Aalto's research plan @ NER H2SIPP

Work Package 2: Pipeline Case-Study

- Supported by the ex-service components from the ***LTU Green fuels*** (@ Piteå, Se) pilot plant:



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Aalto's research plan @ NER H2SIPP

"Hydrogen PIPELINE material selection and integrity control with CASE-STUDY"

Aalto tasks	Hydrogen PIPELINE materials selection and integrity control with CASE-STUDY
Task 1	MATERIAL SELECTION: Selection and characterization of conventional and advanced materials for hydrogen pipeline
Task 2	MATERIAL CHARACTERIZATION: Characterization of hydrogen permeation and desorption via TDS
Task 3	MATERIAL SAFETY: Influence of hydrogen charging in material strength properties
Task 4	NDT PLAN: Laboratorial demo with definition of NDT plan
Task 5	INTEGRATION: Contribution to solutions and processes on knowledge gaps

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Aalto's research plan @ NER H2SIPP

Status on contribution to WP 2: Pipeline Case-Study

- **Diaphragm** sheet metal from sequential 2 step **Hydrogen Diaphragm Compressor** system:
  - **with ≈12 000 h accumulated operation** (operation-campaigns of up to three weeks, and longer)
  - **under 30 to 130 bar of up to 66 vol% of H_2** (in stand-by since 2016)

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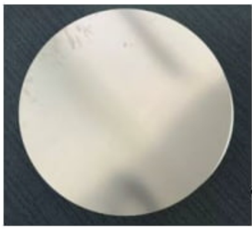
Aalto's research plan @ NER H2SIPP

Status on contribution to WP 2: Pipeline Case-Study

- **Diaphragm** sheet metal from sequential 2-step **Hydrogen Diaphragm Compressor**

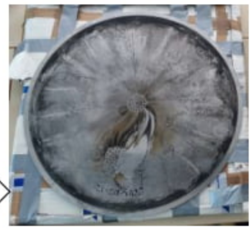


EN 1.4310 (AISI 301) spring-hard stainless-steel

t = 0.5 mm

∅ = **664 mm** and **484 mm**

as-received condition ⇐ ⇒ *ex-service condition*



C	Si	Mn	Cu	Al	Mo	Cr	Ni	V	Ti	Nb	Co	W	Fe
0,09	1.10	0.99	0.17	0.01	0.31	14.99	5.69	0.05	<0.01	0.04	0.20	0.10	76.25

Chemical composition [wt%] via Atomic Emission Mass Spectrometer

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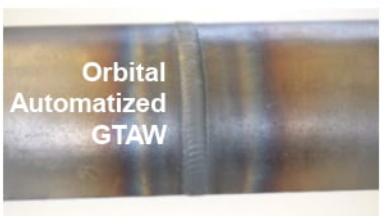
Aalto's research plan @ NER H2SIPP

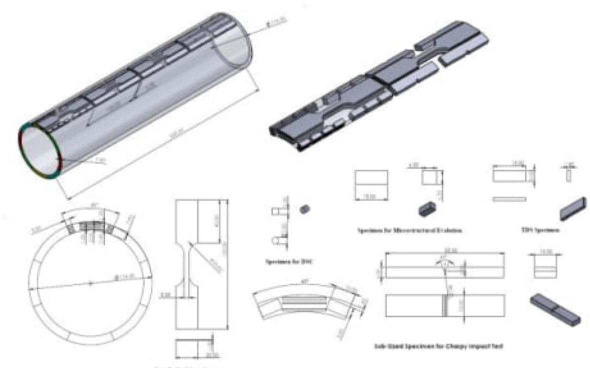
Status on contribution to Task 2: Pipeline Case-Study

Pipeline API 5L X70:



GTAW
- EWTh-2
- FM: ER70S-6; ∅=1.2mm
- 4 passes
  - WTS = 90 to 110 mm/min
  - I (DCEN) = 140 to 160 A;
  - V = 10 to 12 V;

Specimen extraction plan



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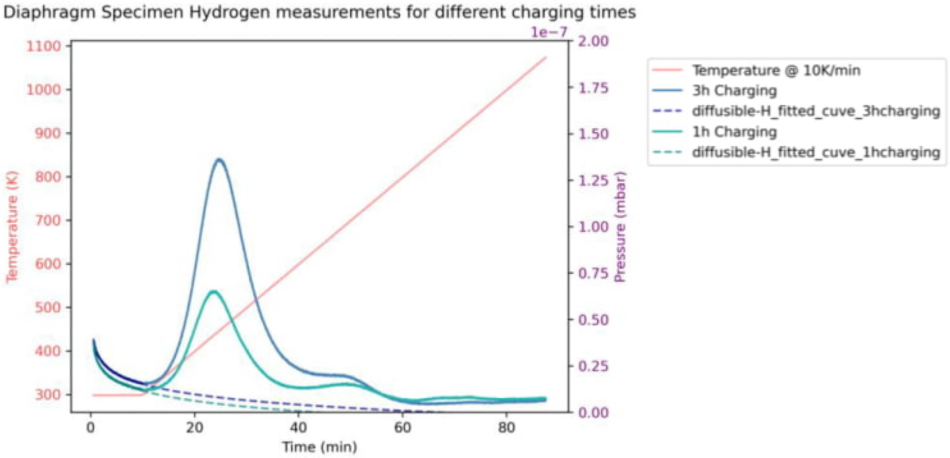
Aalto's research plan @ NER H2SIPP

Status on contribution to Task 2: Pipeline Case-Study

- **TDS analysis of As-supplied Diaphragm Compressor (∅ = 484 mm)**



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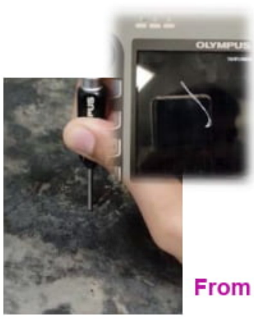
Aalto's research plan @ NER H2SIPP

Status on contribution to Task 2: Pipeline Case-Study

NDT analysis via ET
(eddy currents testing)



From Manual…
…to Automatized dedicated system

Testing Specifications:
- Sampling Frequency = 200 Hz; Angular velocity 7 rpm
- Sampling overlap of more than 50% relative to the probe diameter

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Hydrogen as-a-probe via TDS

…for high-resolution testing of steels

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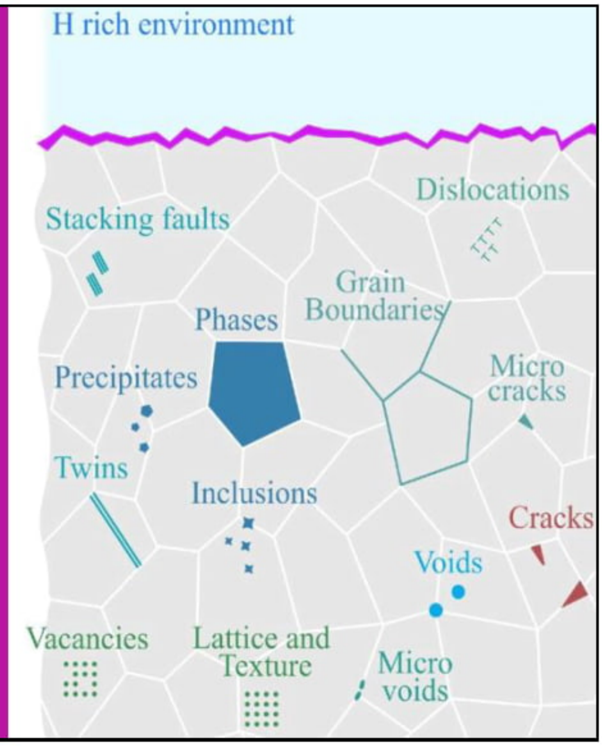

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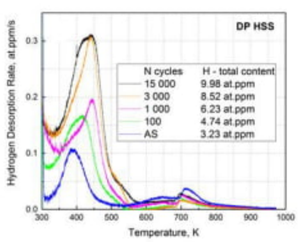
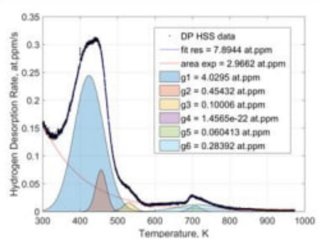
Hydrogen-as-a-probe via TDS

…is a proposed high-resolution and high-sensitive NDT technique for detection of small-scale damage in steels: Fundaments and Methods

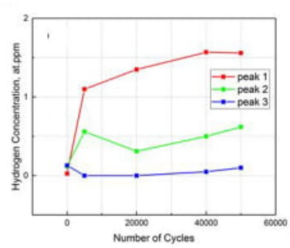
Microstructural defects from fatigue testing referred to the different components of the TDS …this yielded the idea of *using NDT based on hydrogen-as-a-probe*



TDS of hydrogen after fatigue loading in DP HSS



TDS fitting with Gaussian peaks revealing different trapping sites of hydrogen



Evolution of TDS components as a function of fatigue loading cycles

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in E. Malitckii, et al. (2019) **Role of retained austenite in hydrogen trapping and hydrogen-assisted fatigue fracture of high-strength steels.** doi: 10.1016/j.msea.2019.05.103

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Hydrogen-as-a-probe via TDS

…is a proposed high-resolution and high-sensitive NDT technique for detection of small-scale damage in steels: Fundaments and Methods

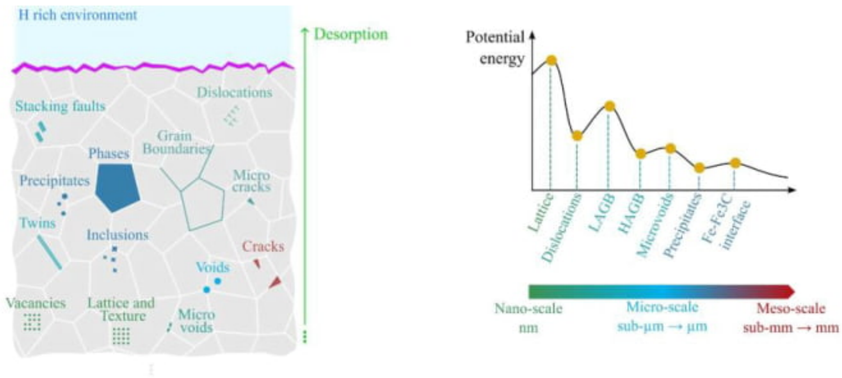

Figure 2 Graphical representation of hydrogen desorption from typical trapping sites in metallic microstructures and respective potential energy levels for hydrogen desorption from those sites

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in M.I.Silva et al. (2024) **Hydrogen-as-a-probe applied to investigate the influence of extraction and preparation methods on TDS spectra of 13CrMo4-5 samples**. doi: 10.1007/s10853-024-10383-3

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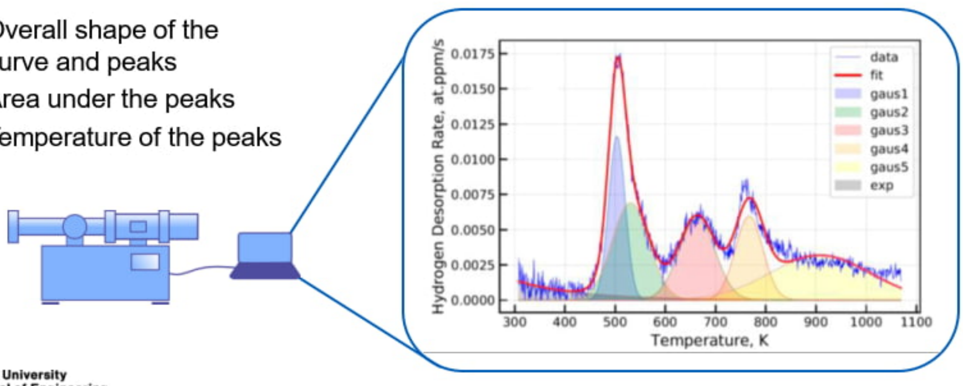
Hydrogen-as-a-probe via TDS

…is a proposed high-resolution and high-sensitive NDT technique for detection of small-scale damage in steels: Fundaments and Methods

enabled by TDS (very) *rich* information

- Overall shape of the curve and peaks
- Area under the peaks
- Temperature of the peaks



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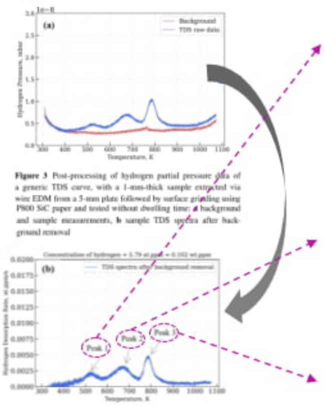
Hydrogen-as-a-probe via TDS

Summary of TDS peaks for 13CrMo4-5 (1Cr-0.5Mo) steel



Peak 1 (≈ 540 K @ 10 K/min) **$E_{activation}$= 51 kJ/mol**

- is associated with low binding energy hydrogen traps with higher intensity NtS, and grows with:
  - Number of dislocations (GND low),
  - Presence of texture effects
  - Number of grain boundaries

Peak 2 (≈ 668 K @ 10 K/min) **$E_{activation}$ = 79 kJ/mol**

- is associated with strong energy hydrogen traps mechanisms, and grows with:
  - Density of NMI's, with H at their interface
  - Content of LAGB, of the slightly larger and softer grain at the middle area of the plate

Peak 3 (≈ 800 K @ 10 K/min) **$E_{activation}$ = 127 kJ/mol**

- is associated with:
  - Carbide precipitation phenomena (e.g. Cr and Mo-rich carbides)

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Hydrogen-as-a-probe via TDS

Analysis of influence of extraction and preparation methods

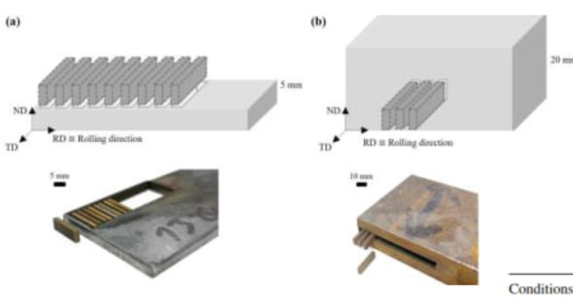
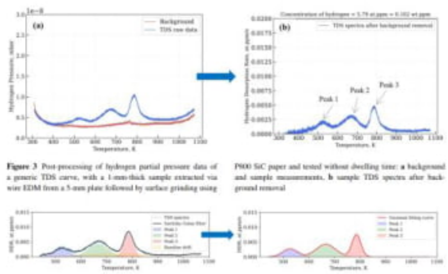


Figure 5 Schematic view of TDS samples extraction plan from the studied 13CrMo4-5 steel plate with **a** 5 mm thickness and **b** 20 mm thickness. For the 5-mm plate, the EDM and MC cutting



Conditions	Peak 1	Peak 2	Peak 3	Total H concentration
Extraction method	No influence	High	No influence	Very high
Surface grinding	No influence	Very high	No influence	Extremely high
Dwelling time	Small	No influence	No influence	Small
Original plate thickness	No influence	Very small	No influence	Small
Sample thickness	Very small	Medium	Small	High

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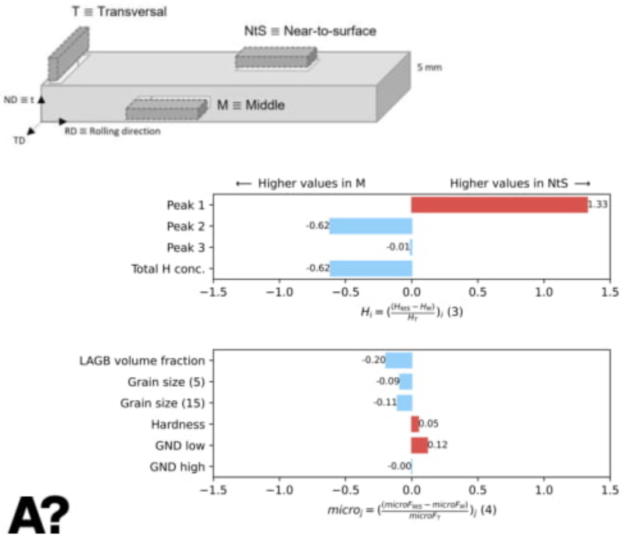
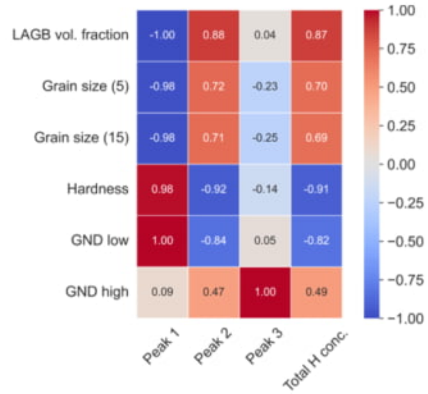
in M.I.Silva et al. (2024) **Hydrogen-as-a-probe applied to investigate the influence of extraction and preparation methods on TDS spectra of 13CrMo4-5 samples**. doi: 10.1007/s10853-024-10383-3

Hydrogen-as-a-probe via TDS

Analysis of influence of sample location





in M.I.Silva et al. (2024) **Influence of sample extraction location on thermal desorption spectroscopy from a heat-resistant 13CrMo4-5 steel plate and correlation with microstructure features.** doi: 10.1016/j.mtla.2024.102130

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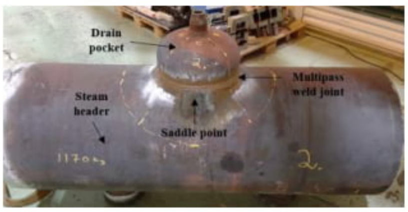
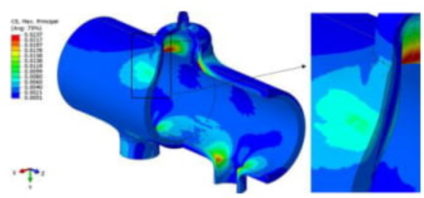
Hydrogen-as-a-probe via TDS

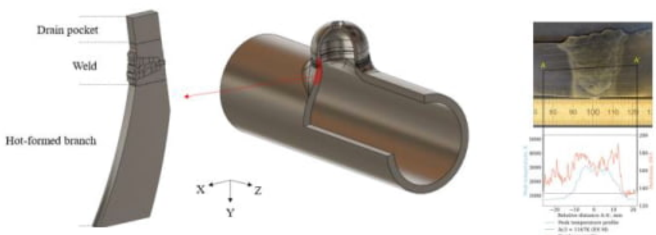
…to access imperfections of 13CrMo4-5 ex-service steel component





Ex-service steam-header (> 3 decades @ power plant):

- **~290 000 h @ 783 K / 60 bar**
- **13CrMo4-5 (1Cr-0.5Mo) normalised and aged**
- **includes a hot-formed branch opening for a welded drain pocket section**



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in M.I.Silva et al. (2024) **Application of hydrogen-as-a-probe to access the metallurgical condition and imperfections of a 13CrMo4-5 ex-service steel component.** in preparation and reviewing

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New concept and design of fuel cells (electrolyzers)

…enabled by Aalto's innovation in manufacturing

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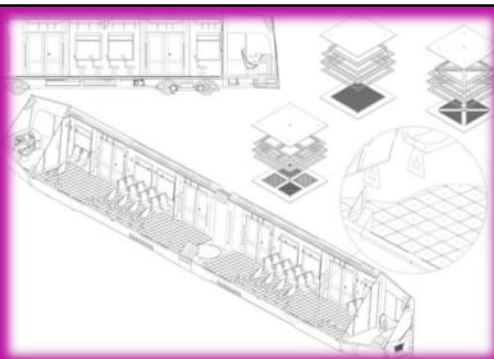

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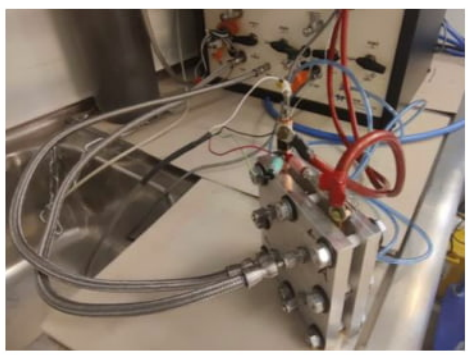
New concept of Fuel Cells/Electrolyzers

Setting grounds for comparative performance evaluation (Electrical, Chemical, Mechanical)

Evaluation of influence in operation of:
- Al-based electrodes
- Thermal management
- ➢ Result: Operational conditions versus
  - ✓ Al-based electric performance and Al-based power density (kW/Kg)

Standard single **Fuel Cell made at Aalto** (squared shape)



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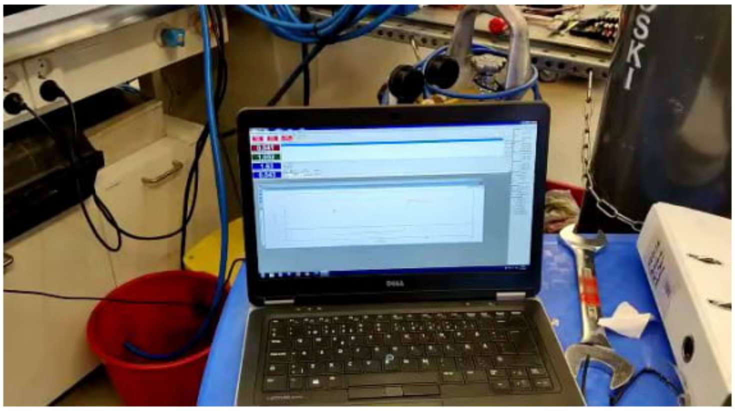
New concept of Fuel Cells/Electrolyzers

Setting grounds for comparative performance evaluation (Electrical, Chemical, Mechanical)

It works!



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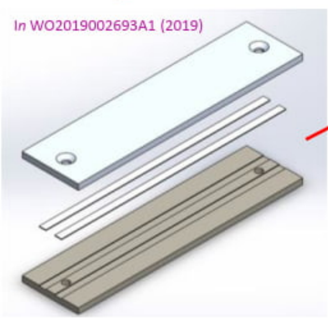
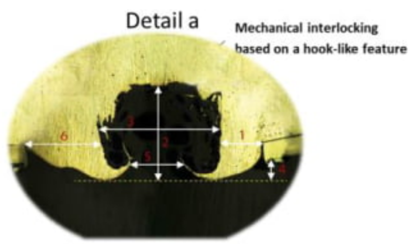
New concept of Fuel Cells/Electrolyzers

… enabled by Aalto's innovation in manufacturing: TSEJ

TSEJ ≡ Through Slot Extrusion Joining



***claw-like* feature (mechanical interlocking)**



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in Welding in the World (2024) doi: 10.1007/s40194-023-01622-3

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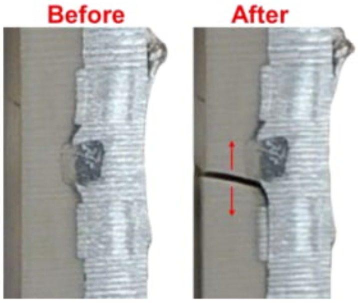
New concept of Fuel Cells/Electrolyzers

... enabled by Aalto's innovation in manufacturing: TSEJ



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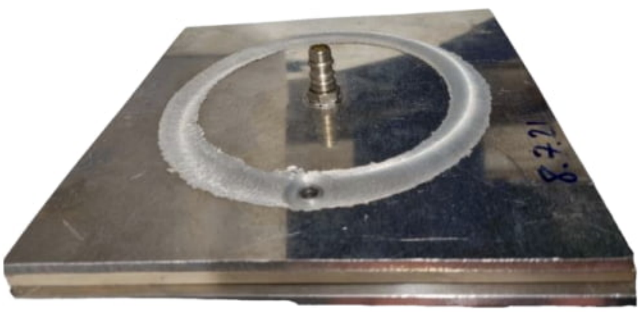
New concept of Fuel Cells/Electrolyzers

... enabled by Aalto's innovation in manufacturing: TSEJ



Successful gas-tight leak test done (19/08/2020)

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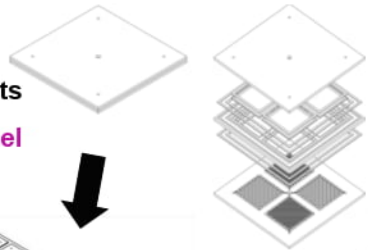
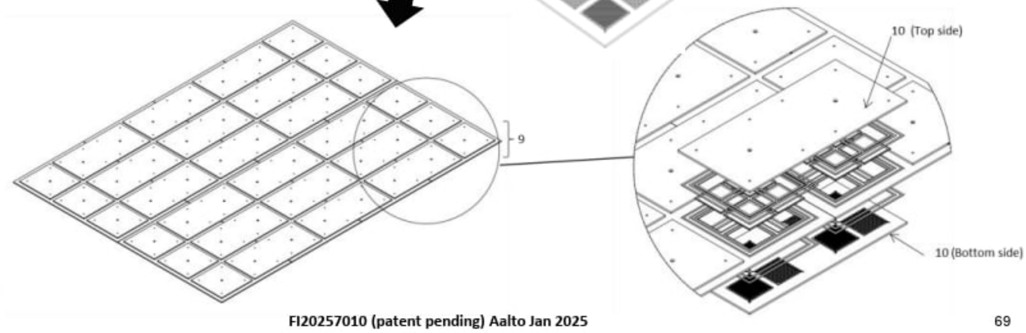
New concept of Fuel Cells/Electrolyzers

Bipolar multicell panel-based design of PEM FC/E

FI20257010 (patent pending) Aalto Jan 2025



from Polar Multicell units
to Bipolar Multicell Panel



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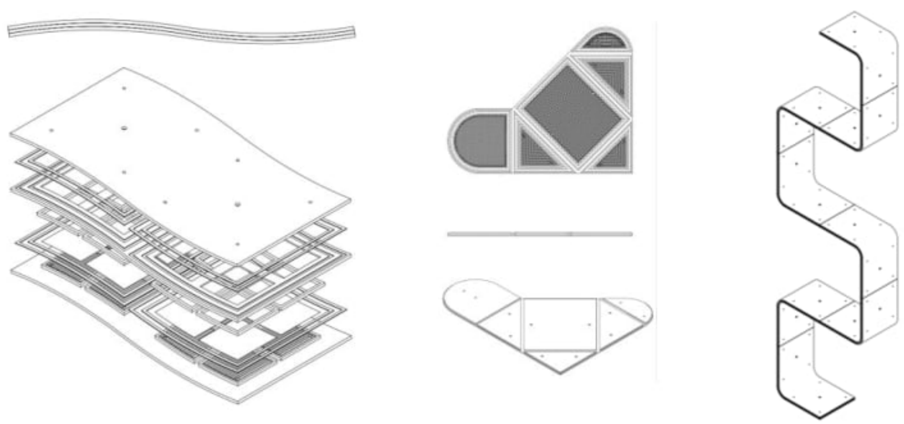
FI20257010 (patent pending) Aalto Jan 2025

New concept of Fuel Cells/Electrolyzers

Bipolar multicell FREE-SHAPE panel-based design of PEM FC/E



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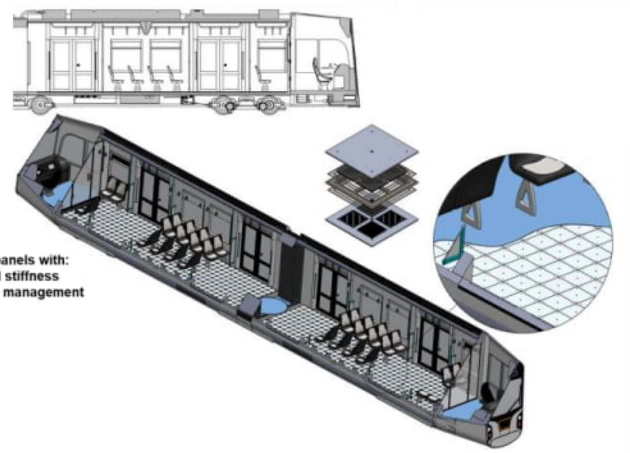
FI20257010 (patent pending) Aalto Jan 2025

New concept of Fuel Cells/Electrolyzers

Bipolar multicell panel-based design of PEM FC/E

Integrated panels with:
- structural stiffness
  + thermal management



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New concept of Fuel Cells/Electrolyzers

Bipolar multicell panel-based design of PEM FC/E

Integrated panels with:
- structural stiffness
  + thermal management

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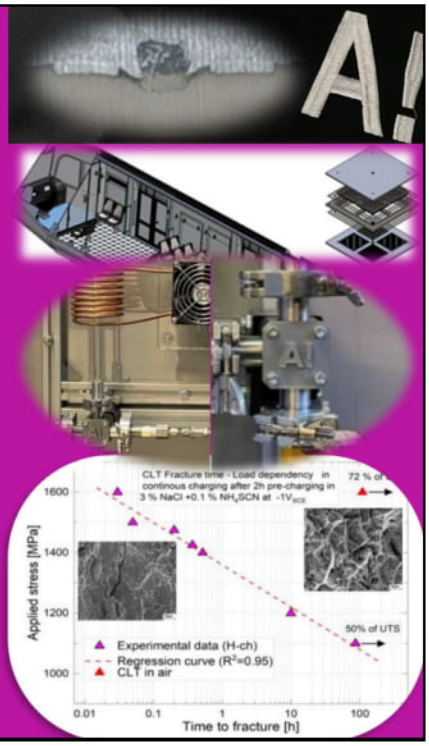
FI20257010 (patent pending) Aalto Jan 2025

Final Remarks

at Aalto's, with
***Materials Safety Analysis* and**
Advanced Manufacturing Technology
we aim at shaping the
Hydrogen Technology
in the world



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Thank you

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Department of Energy and Mechanical Engineering
Materials and Manufacturing to Products (M2P) Research Group

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