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Tekniker
Researcher

EVALUATION OF HYDROGEN PERMEABILITY AND EMBRITTLEMENT IN CRITICAL COMPONENTS FOR H_2 SUPPLY SYSTEMS

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Tekniker
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

ModHEATech
Modular HEATing Technology through renewable resources for steel production

European Commission

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement N°101092234

ESTEP
DIGIMET
DANIELI AUTOMATION
UNIVERSITÀ DEGLI STUDI DI UDINE
HIC SUNT FUTURA

WHO WE ARE

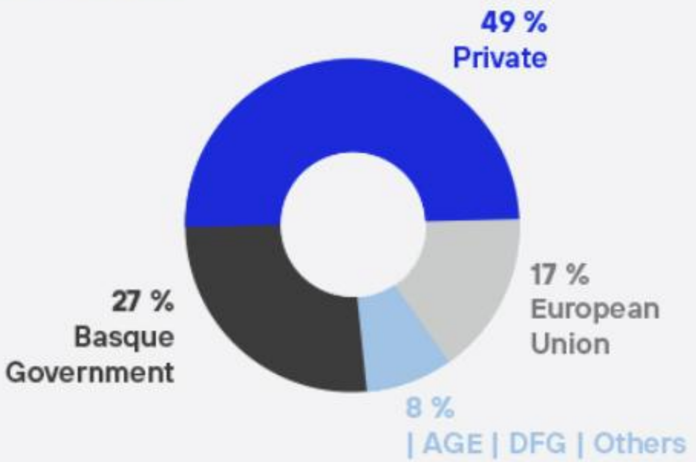
R&D Centre
(not-to-profit Private Foundation) |
Applied research spanning 44 years

Our misión is to deliver growth and wellbeing to society at large via R&D&I and to further the competitiveness of the business fabric in a sustainable manner

Specialised in **Manufacturing**

TOTAL REVENUE TEKNIKER
33,2 M€

R&D revenue



PLEOPLE TEKNIKER
303

37% Women
63% Men

PhD Resources
78 doctors
23 doctoral students

83% university degress

DATA 2024

CURRRENT PORTFOLIO OF SHAREHOLDINGS IN COMPANIES

Atten[2] Deep monitoring solutions
masermic
GMTK MAHER HOLDING
GOIALDE HIGH SPEED
H2GREEM GLOBAL SOLUTIONS
i-TRIBOMAT THE EUROPEAN TRIBOLOGY CENTRE

TOTAL REVENUES IN INVESTED COMPANIES
14,6 M€

PEOPLE IN INVESTED COMPANIES
70

TOTAL REVENUE **TEKNIKER + INVESTED COMPANIES**
47,8 M€

PEOPLE **TEKNIKER + INVESTED COMPANIES**
373

TEKNIKER IN FIGURES

INDUSTRIAL PROJECTS

160 | Ongoing

START-UP´S

32 | Companies established

PATENTES

118 | Patests families

357 | Patents

3 | First filings 2024

11 | Exploited patents 2024

DISTINCTION | PUBLICATIONS

54 | 2024 Indexed publications

23 | Scientific publications in Q1

32 | Publications in collaboration with RVCT agents

EUROPEAN PROJECTS

HISTORY

302 | Projects

36 | Years of experience

20 % | Led projects

5,9 M€ | Annual average income

Materials Characterization in presence of hydrogen

Hydrogen embrittlement (HE) is a phenomenon responsible for the **unpredictable** and **premature failure** of metallic materials. This type of hydrogen damage is directly related to the phenomena of hydrogen diffusion and hydrogen trapping inside the material.

Interactions between hydrogen atoms and metal microstructure. **Electrochemistry and gas**

Applications: transport, storage

Deterioration of the mechanical properties of the material due to H_2 entering the crystal lattice. **ISO 11114-4**

Applications: transport, storage

Hydrogen combustion results in **higher operating temperatures** and **higher water vapor** contents than other processes.

Oxidation/corrosion processes

Applications: Hydrogen combustion furnaces/chambers

Hydrogen leak detection proof of concept using forming gas as tracer gas

Dinamic testing in presence of hydrogen. Joint and seal behavior in H2

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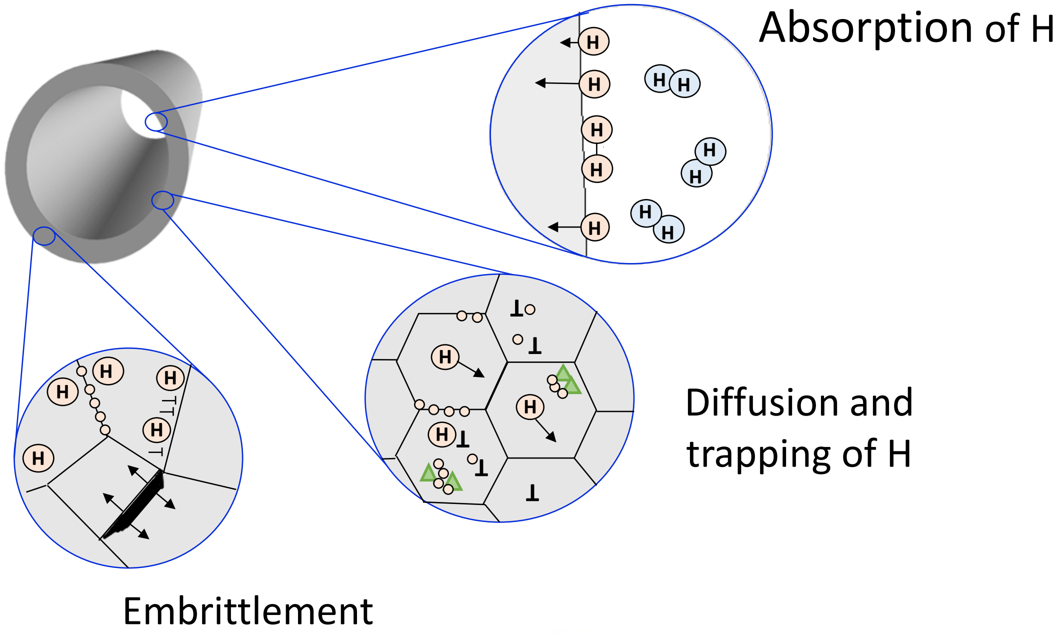
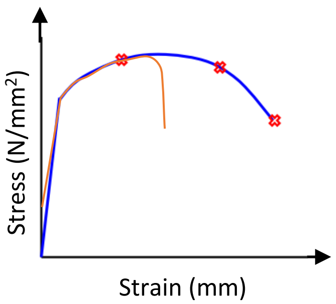
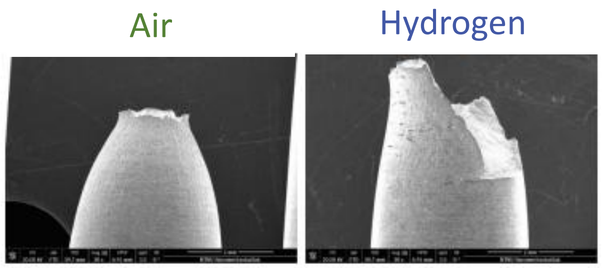
Introduction

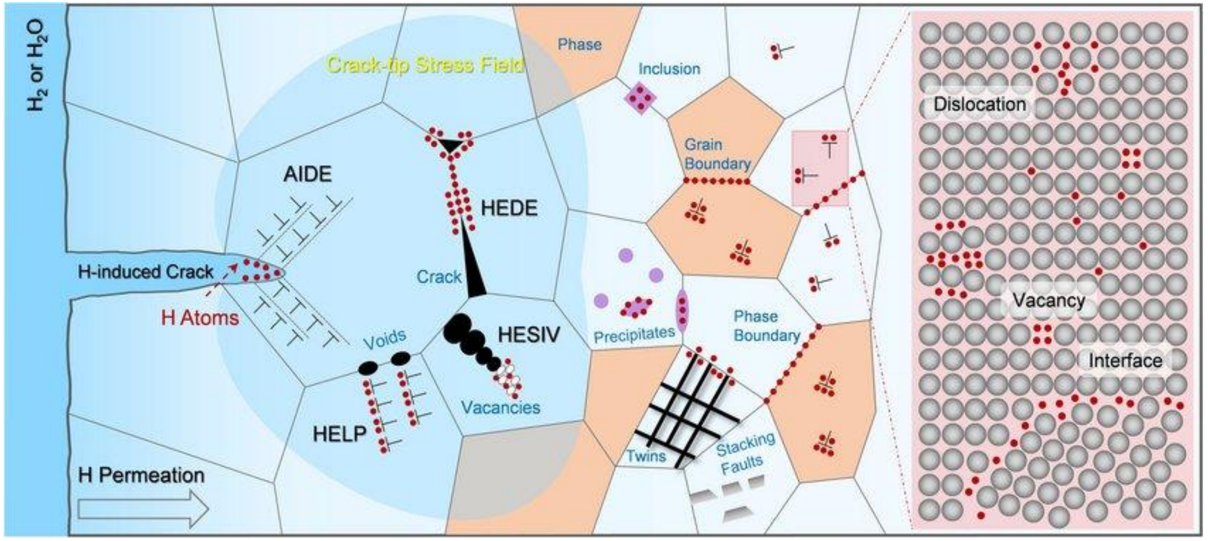






Different embrittlement mechanism

- Hydrogen pressure theory (HPT)
- Hydrogen-enhanced decohesion mechanism (**HEDE**)
- Adsorption-induced dislocation emission (**AIDE**)
- Hydrogen-enhanced local plasticity (**HELP**)
- Hydrogen-enhanced strain-induced vacancy formation (HESIV)



B. Sun, "Hydrogen Embrittlement in High-Performance Alloys" Max Planck Institute

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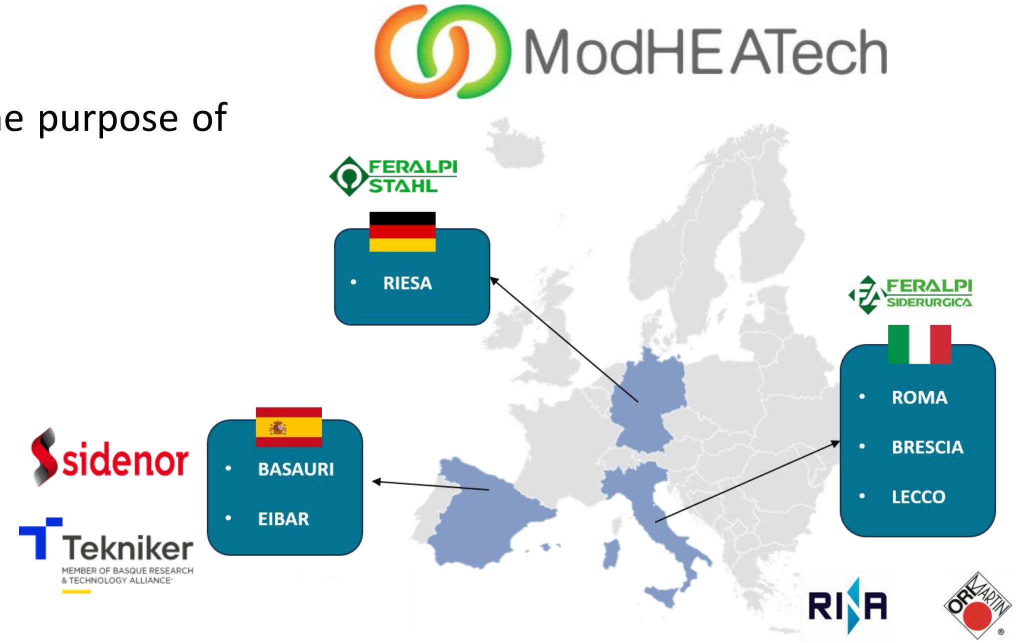
Objectives

Analyse the interaction of **hydrogen** with different **metallic materials**, with the purpose of evaluating them for their application in **hydrogen distribution systems**.



01 **Characterisation** of the selected steals

02 Analyse the **test parameters** of the DS technique

03 Study the **diffusivity and permeability** of hydrogen in steels

04 Analyse the **absorption capacity** and the **trapping** phenomenon

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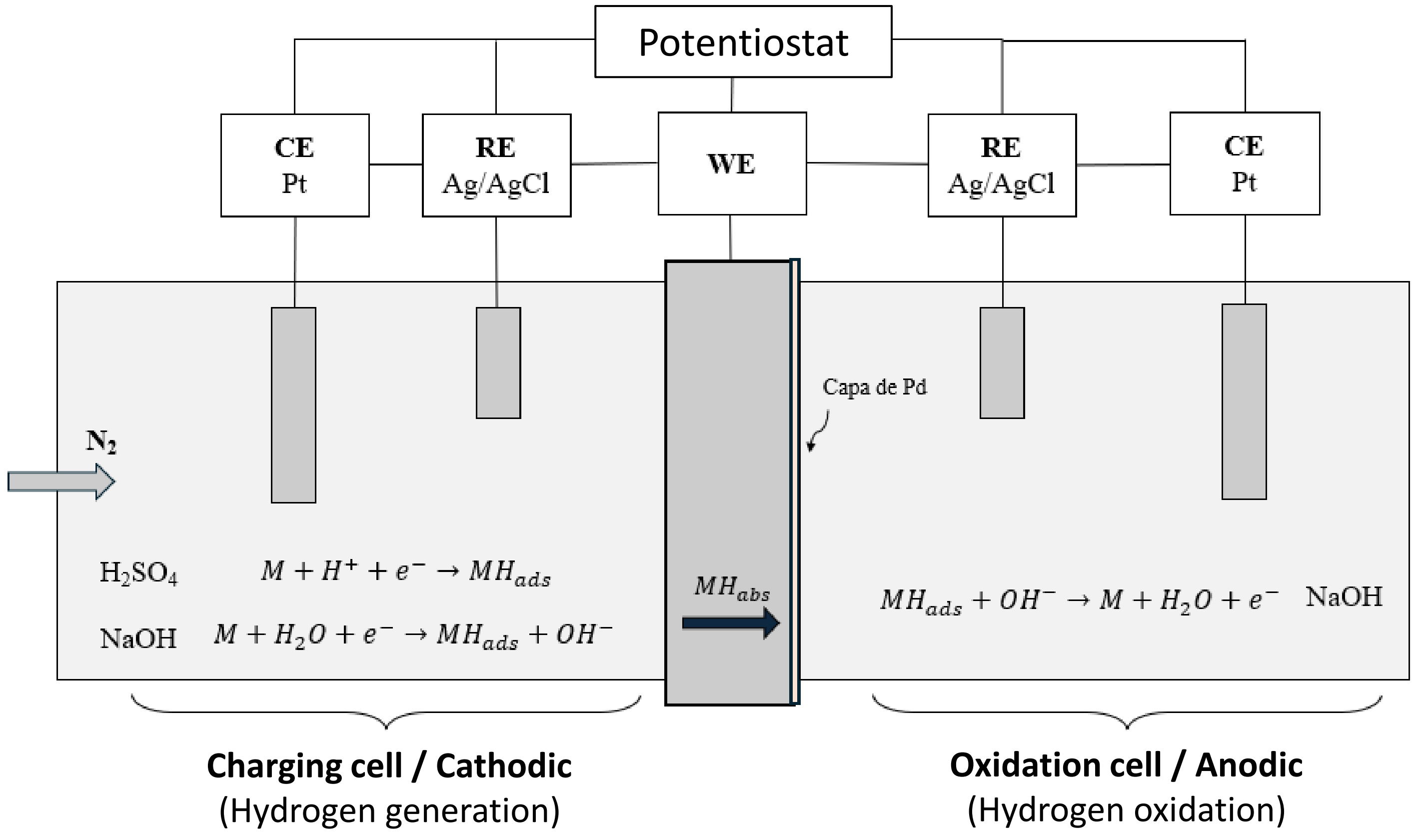
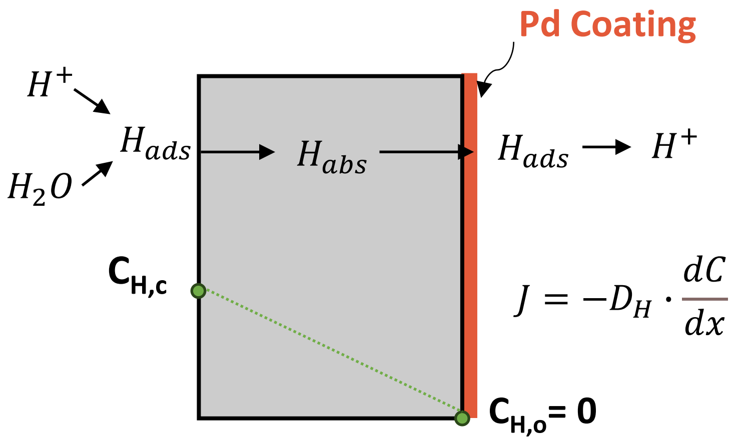
Methodology

Electrochemical Hydrogen Permeation



Determine D_{app} y P_{app}

- Devanathan-Stachurski Electrochemical cell
- Standard ISO 17081:2014
- Metal sheet located between the load and oxidation cells



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Methodology

Electrochemical Hydrogen Permeation

1 → **Palladium Deposition**

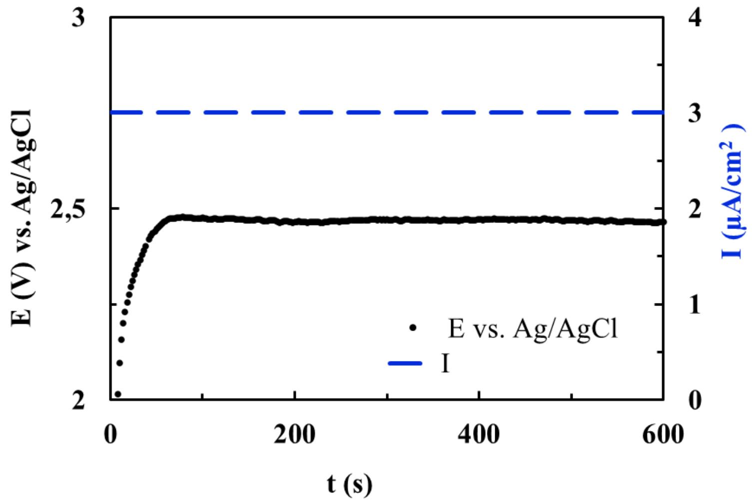
3 mA/cm² during 10 min

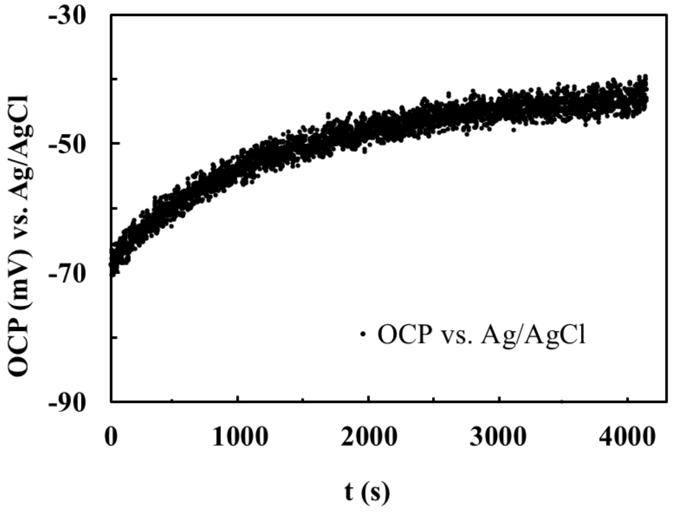
2 → **OCP & Stabilisation**

Between -40 and -50 mV

$I_{ss} < 0.1$ µA/cm²

3 → **Hydrogen charging**





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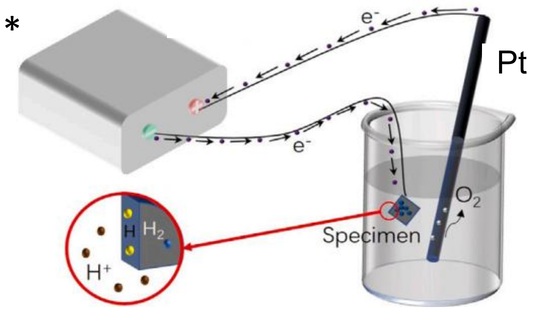
Methodology

Thermal Desorption Spectroscopy (TDS)

Evaluate the absorption capacity and the trapping phenomenon

1 **Electrochemical precharging of hydrogen**



2 **Determine desorbed hydrogen**

G4 PHOENIX DH

After precharging (Absorption capacity)

After **different** t_{exp} (Trapping phenomena)

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* Zafra, A., et al. (2022). Comparison of hydrogen diffusivities measured by electrochemical permeation and temperature-programmed desorption in cold-rolled pure iron. *Journal of Natural Gas Science and Engineering*, 98, 104365.

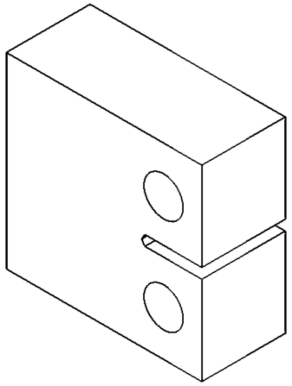
Methodology

Hydrogen embrittlement characterisation

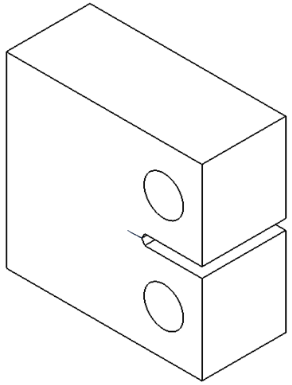
Specifies the test methods and evaluation results for qualifying steels suitable for the manufacture of gas cylinders (up to 3000 l) for hydrogen and other embrittled hydrogen gases.

Method B → Determination of the stress intensity factor (k_{IH}) for the cracking susceptibility of metallic materials in contact with hydrogen gas.

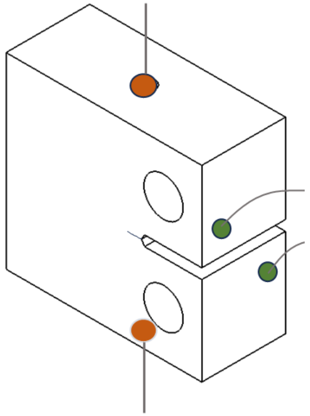
CT Specimen



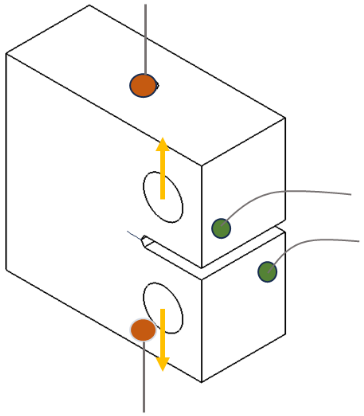
Precracking



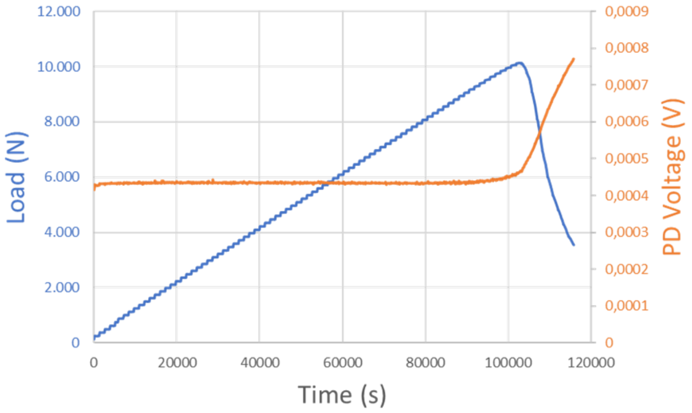
DCPD Conections



Test (P=80 bar)



ISO 11114-4 method B



- Apply load equivalent to k_I=1 MPa·$m^{0,5}$
- Maintain 20 min

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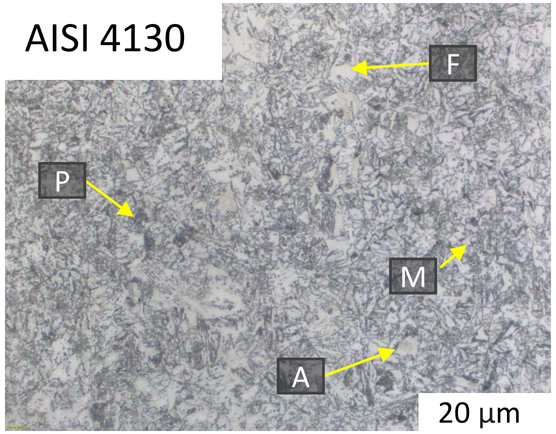
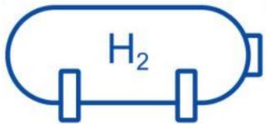
Material Selection

Microstructure	**OM and SEM**
Crystalline Structure	**DRX**
Chemical compositon	**XRF/LECO-CS/EDS**
Roughness	**Confocal Microscopy**

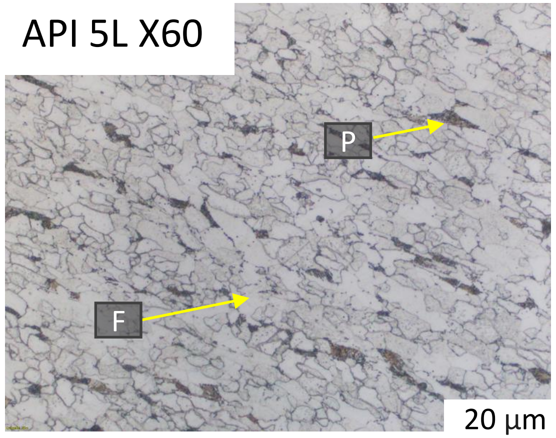
AISI 4130



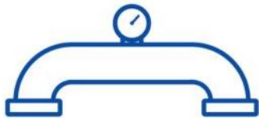
Low-alloy steel Cr-Mo



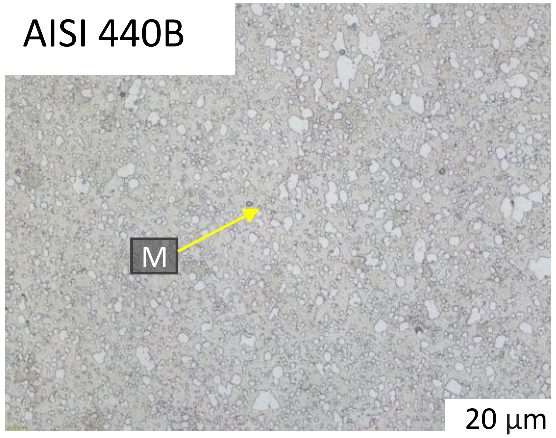
API 5L X60



Pipe Steel



AISI 440B



Stainless Steel

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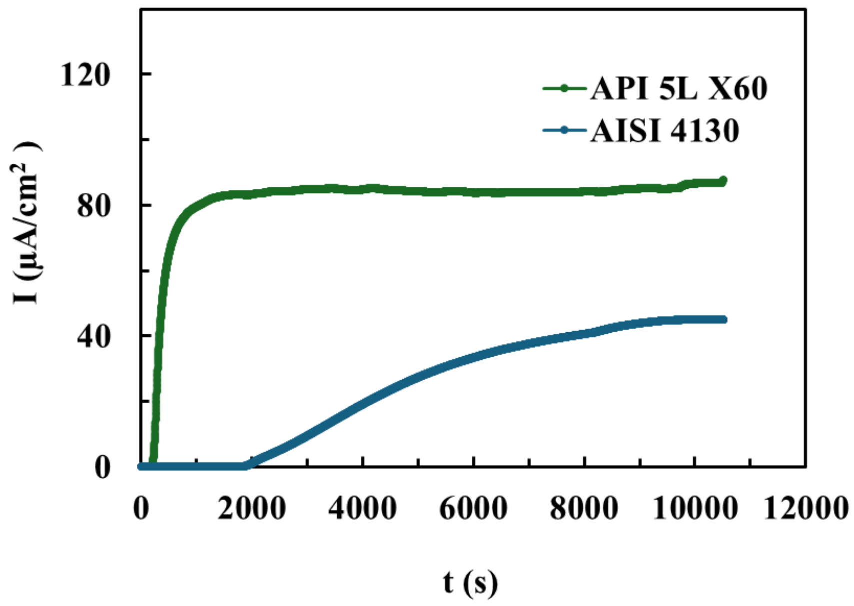
Results and Discussion

Electrochemical Hydrogen Permeation



	D_{app} (10^{-11} m^2 s^{-1})	C_{app} (mol m^{-3})	P_{app} (10^{-10} mol m^{-1} s^{-1})	N_t (10^{-20} cm^{-3})
AISI 4130	5.4 ± 0.01	84.4± 8.4	45.8 ± 0.3	22.6 ± 0.2
API 5L X60	85.2 ± 1.9	9.5± 1.2	87.8 ± 0.9	0.1 ± 0.6

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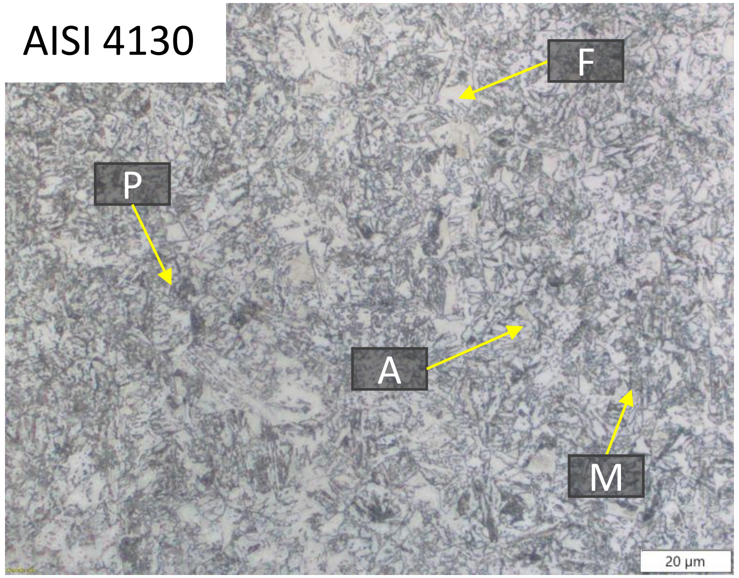
Results and Discussion

Electrochemical Hydrogen Permeation

AISI 4130



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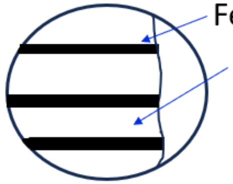
Difference of an order of magnitude

AISI 4130

- **"Complex" microstructure** → Numerous phase boundaries
- **Martensite** → Deffects and dislocations
- **Retained Austenite γ (FCC)** → S of hydrogen ↑ / D of hydrogen ↓ } Able to absorb and retain H
- **Interphases γ/α**
- **Perlite (Interphase α/Fe_3C)** } Irreversible trapping



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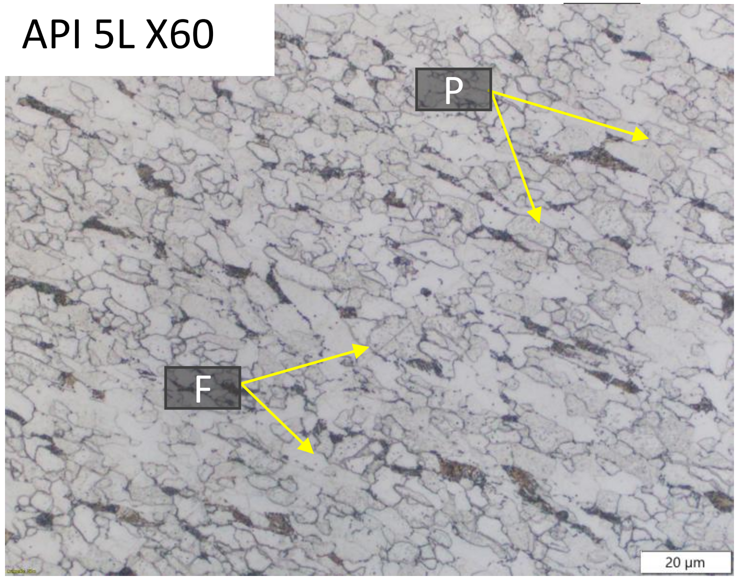
Results and Discussion

Electrochemical Hydrogen Permeation

API 5L X60



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API 5L X60	**85.2 ± 1.9**	**9.5± 1.2**	**87.8 ± 0.9**	**0.1 ± 0.6**

Difference of an order of magnitude

API 5L X60

- **"Simple" microestructure** ⟶ Less phase boundaries

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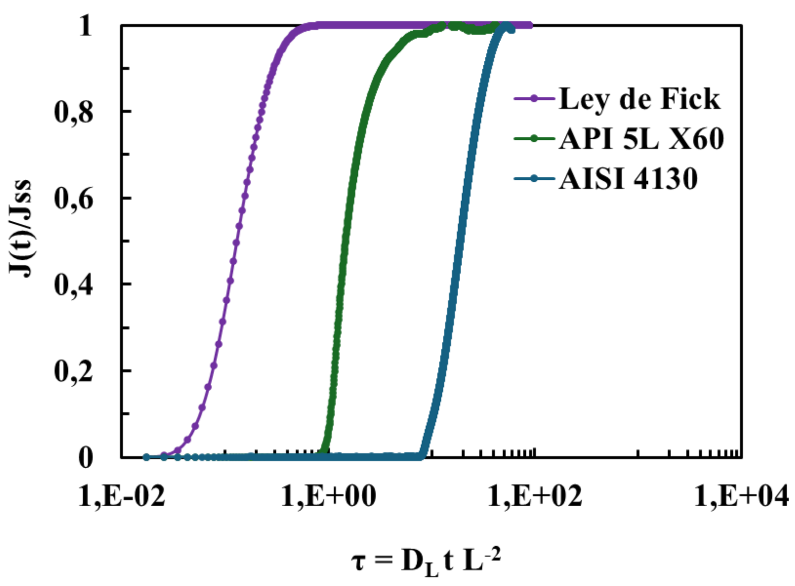
Results and Discussion

Electrochemical Hydrogen Permeation



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API 5L X60	85.2 ± 1.9	9.5± 1.2	87.8 ± 0.9	0.1 ± 0.6

Reverse trend — similar P_{app} — Difference of two orders of magnitude

AISI 4130 y API 5L X60

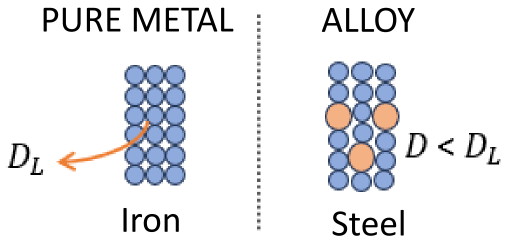
- **Trapping phenomena**

Effects → D_{app} ↓, C_{app} ↑

$$P_{app} = C_{app} \cdot D_{app}$$

- **Prediction of Fick's second law**

AISI 4130 higher shift



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Results and Discussion

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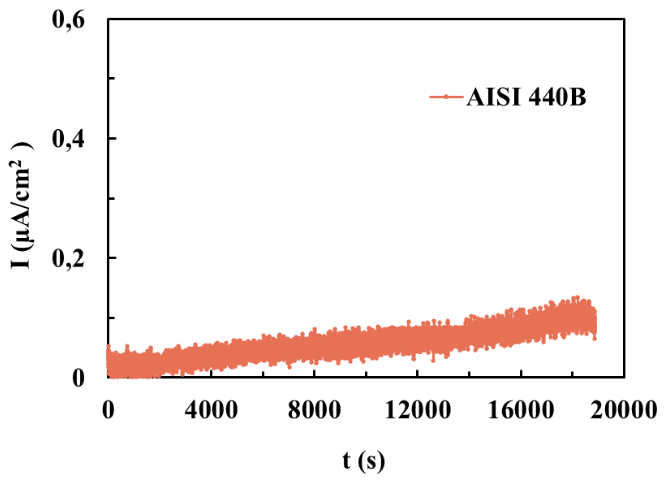

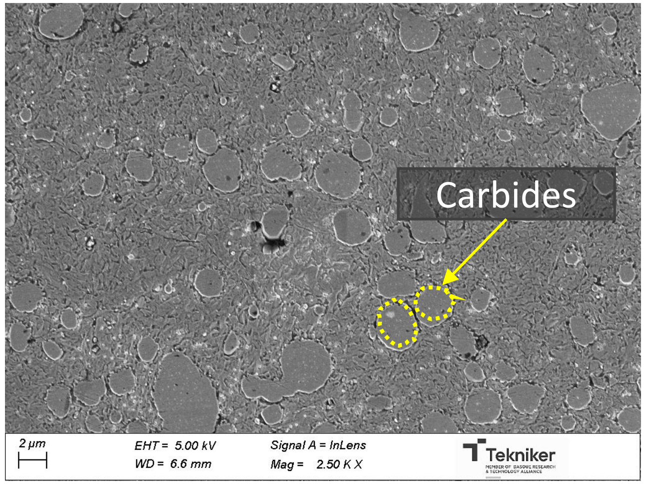

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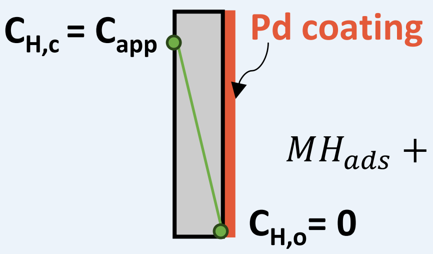
API 5L X60	85.2 ± 1.9	9.5± 1.2	87.8 ± 0.9	0.1 ± 0.6
AISI 440B**	**0.9 ± 0.3**	**1.7± 0.5**	**0.1 ± 0.5**	**2.6 ± 0.7**

AISI 440B

- **Martensite** → Deffects and dislocations
- **Chromium carbides** → Irreversible trapping

**** Importance of Pd deposition**



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

- Catalyzes the oxidation reaction
- Avoids recombination

⇩

Apparent reduction in permeation rate

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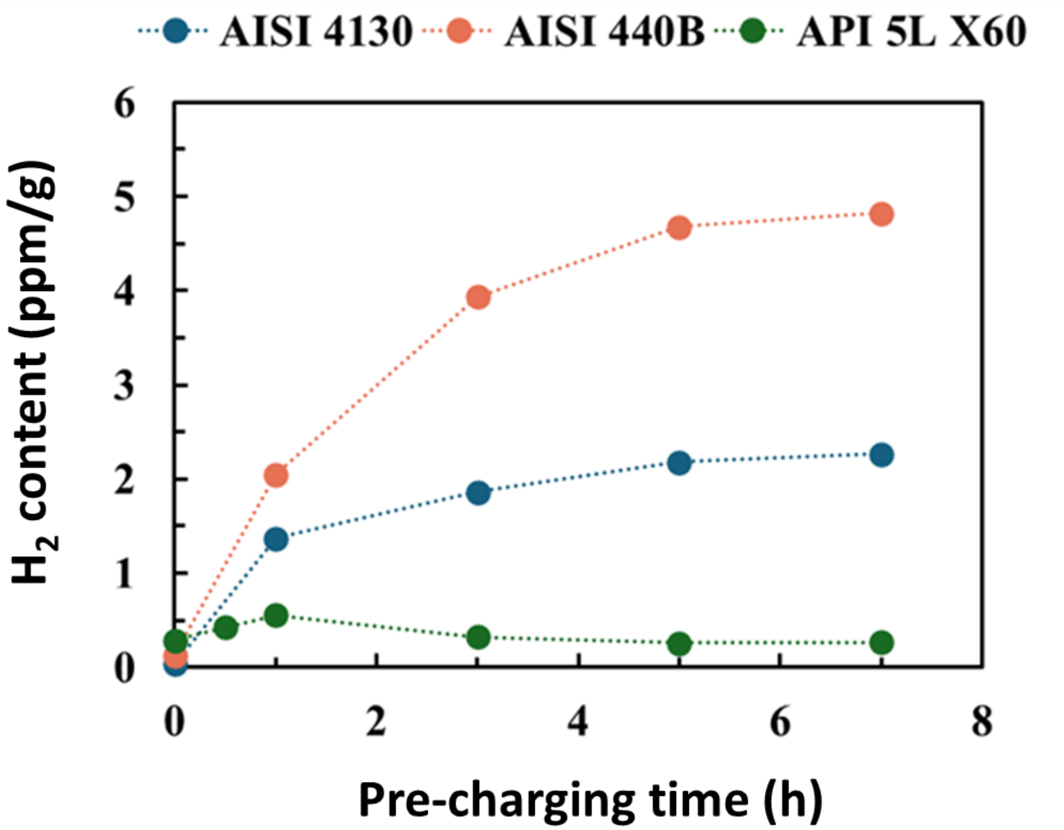
Results and Discussion

Electrochemical Hydrogen Permeation



- For the same charging conditions of H_2

  AISI 440B > AISI 4130 > AISI 5L X60

- Trapping ↑ Apparent Solubility↑

- Importance of **trapping nature**

Reversibles (Majority in AISI 4130)

Irreversibles (Majority in AISI 440B)

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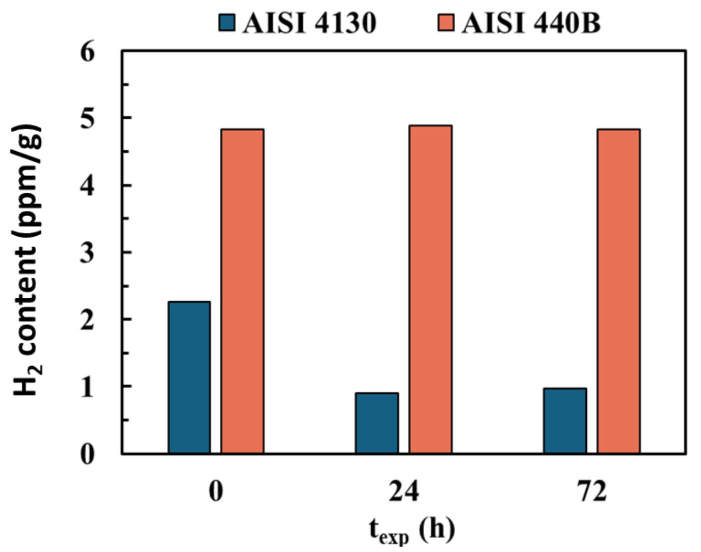
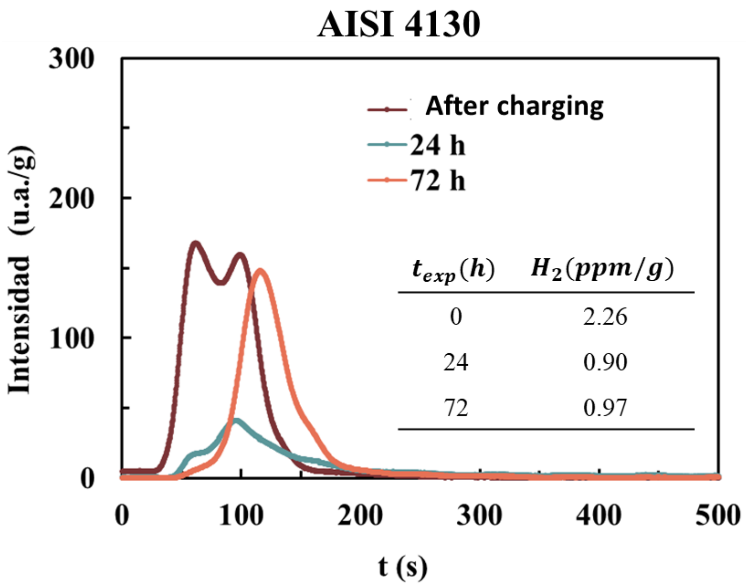
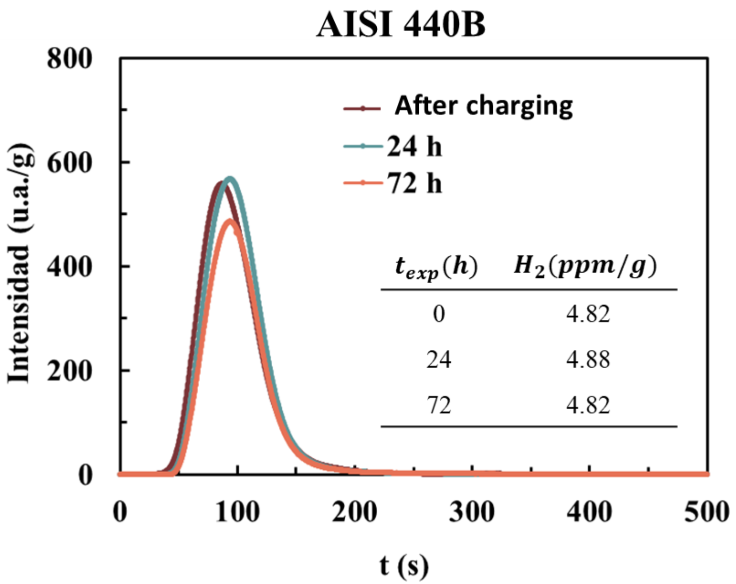
Results and Discussion

Hydrogen absorption properties







Reversible (majority in **AISI 4130**) → H_2 desorbs at **RT**
Irreversible (majority in **AISI 440B**)→ **Require T** to be desorbed

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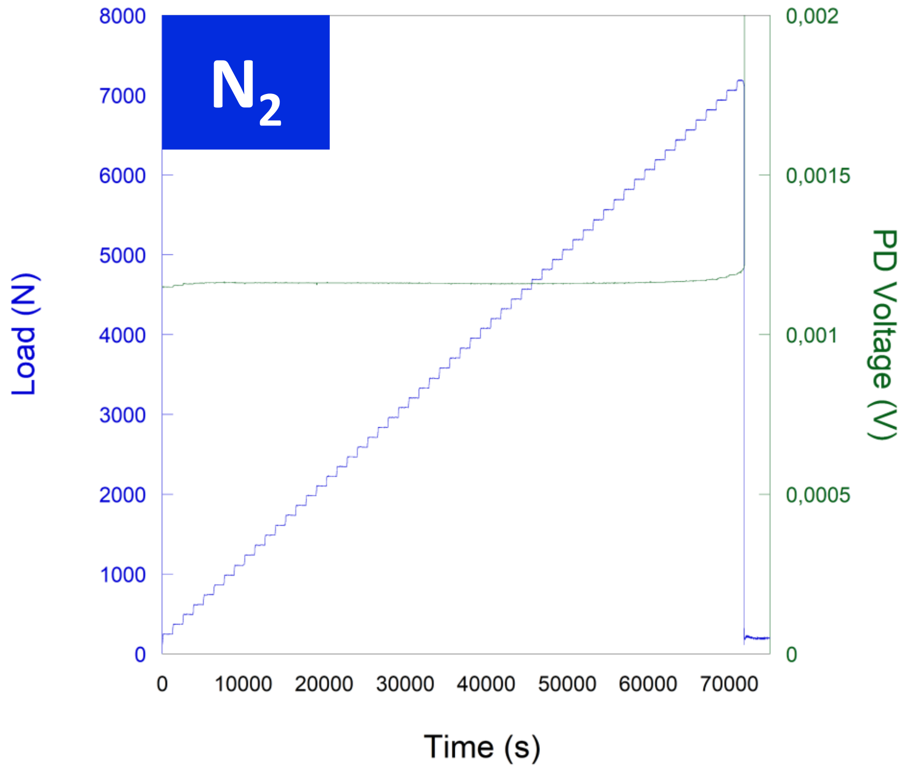
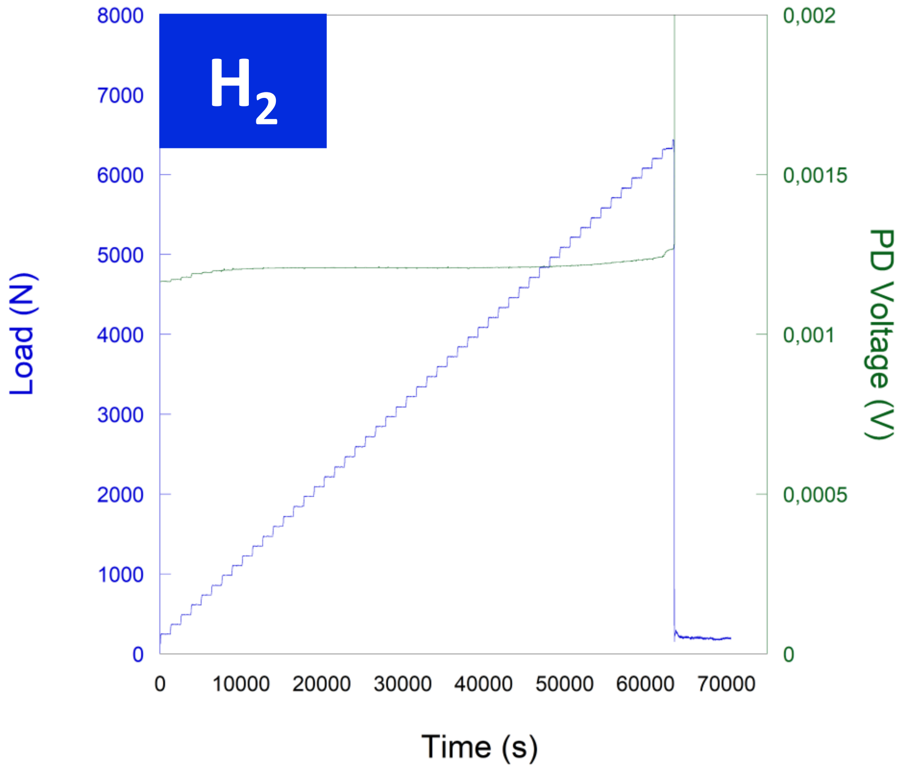
Results and Discussion

Hydrogen embrittlement





Atmosphere	F_{max} (kN)	$t_{\Delta DCPD}$ (s)	$F_{\Delta DCPD}$ (kN)	K_I test ($MPa \cdot m^{0,5}$)	K_{IH} ($MPa \cdot m^{0,5}$)
N_2	7,19	71200	7,18	57	56
H_2	6,44	54500	5,55	44	42

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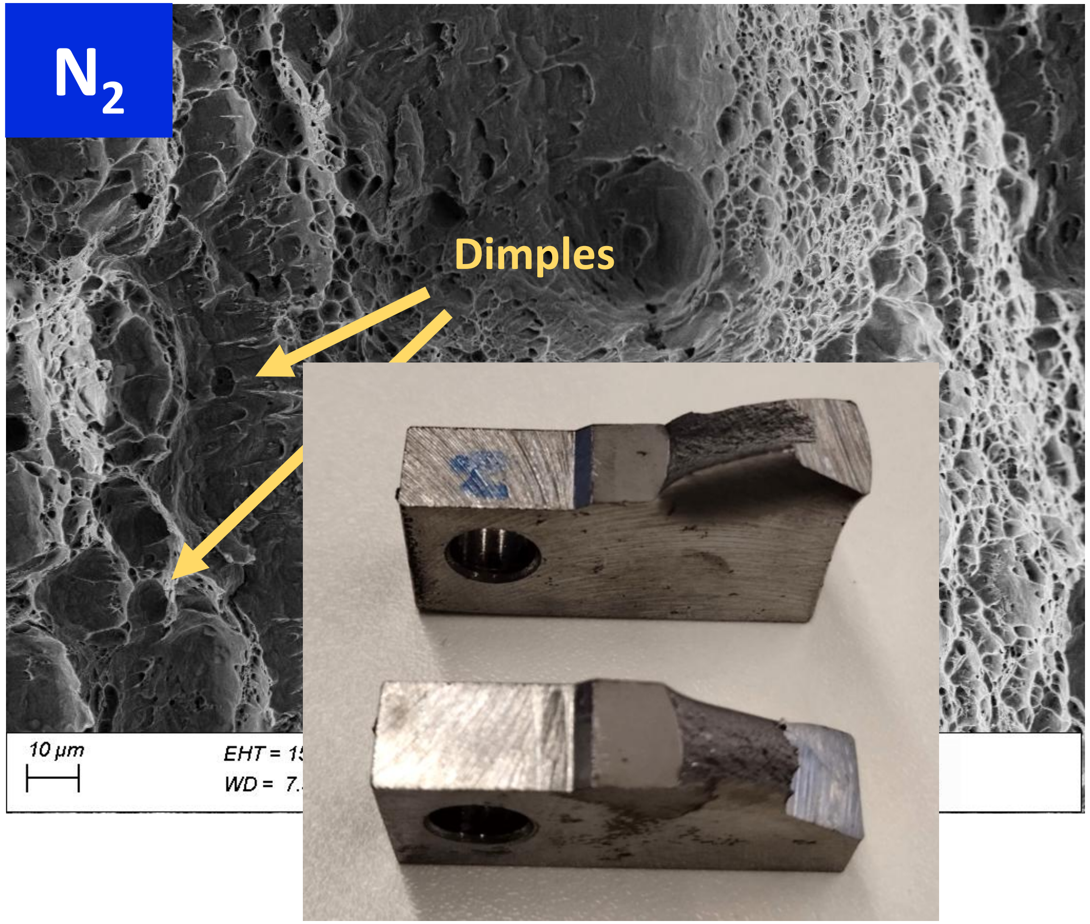
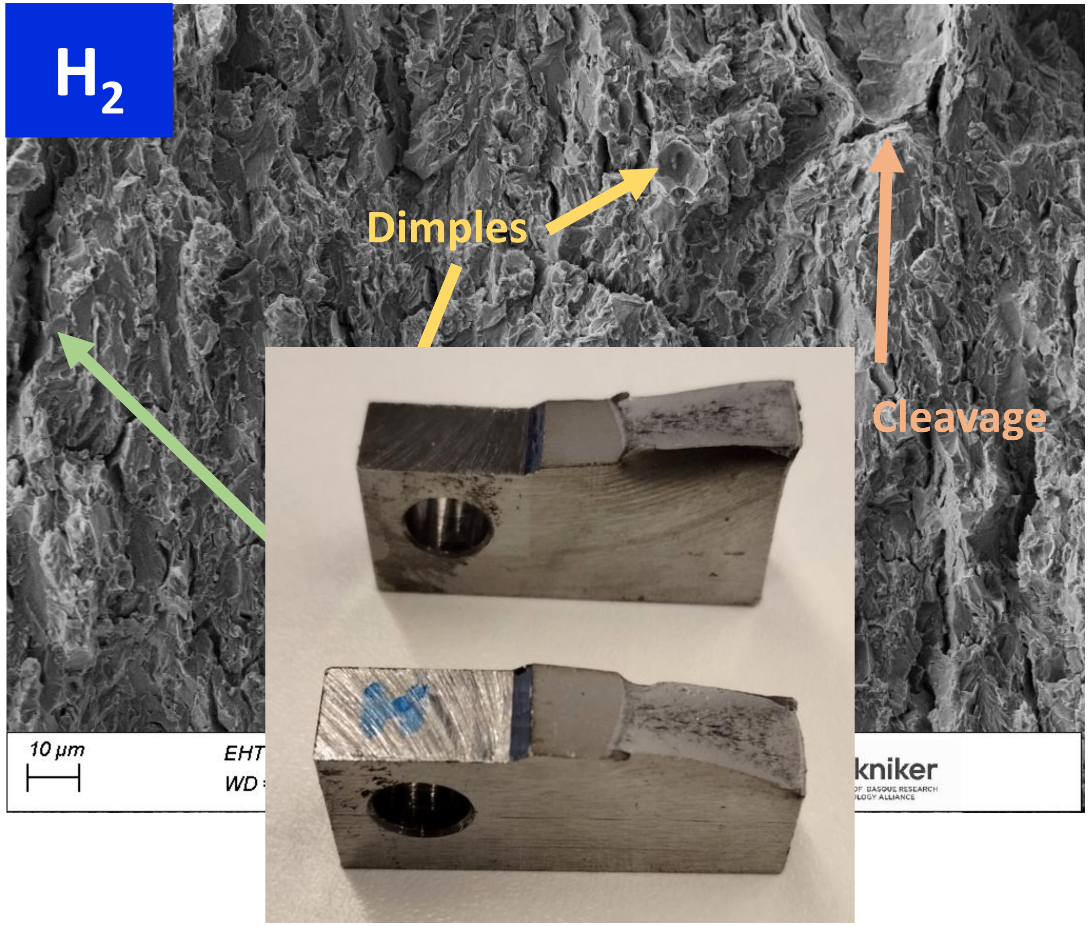
Results and Discussion

Hydrogen embrittlement



Ductile Fracture



Brittle Fracture

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Conclusions

Interaction of hydrogen with materials – Permeability and hydrogen uptake

1. **Complex microstructures hinder hydrogen mobility** due to a **greater number of hydrogen traps**. In contrast, **simple microstructures favor hydrogen diffusion**.

2. **Greater trapping** means D_{app} ↓ **and** C_{app} ↑, which can absorb and retain a **greater number of hydrogen atoms**.

3. **Reversible trapping** by dislocations, grain boundaries, and interfaces between martensite slabs is **predominant in AISI 4130** steel.

4. **Chromium carbides** in **AISI 440B** steel act as **irreversible hydrogen traps**, preventing their desorption at room temperature.

Hydrogen Embrittlement

1. Hydrogen embrittlement effect has been observed in AISI 440B material, with a **25% reduction of the stress intensity factor**

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#GrowthMakers

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