

homogénéisation du comportement mécanique des matériaux hétérogènes

**27-31 janvier 2025**

# L'hydrogène dans les matériaux métalliques : Couplage diffusion-mécanique-microstructure

A. Oudriss, J. Bouhattate, X. Feugas

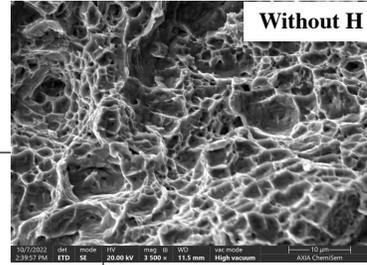
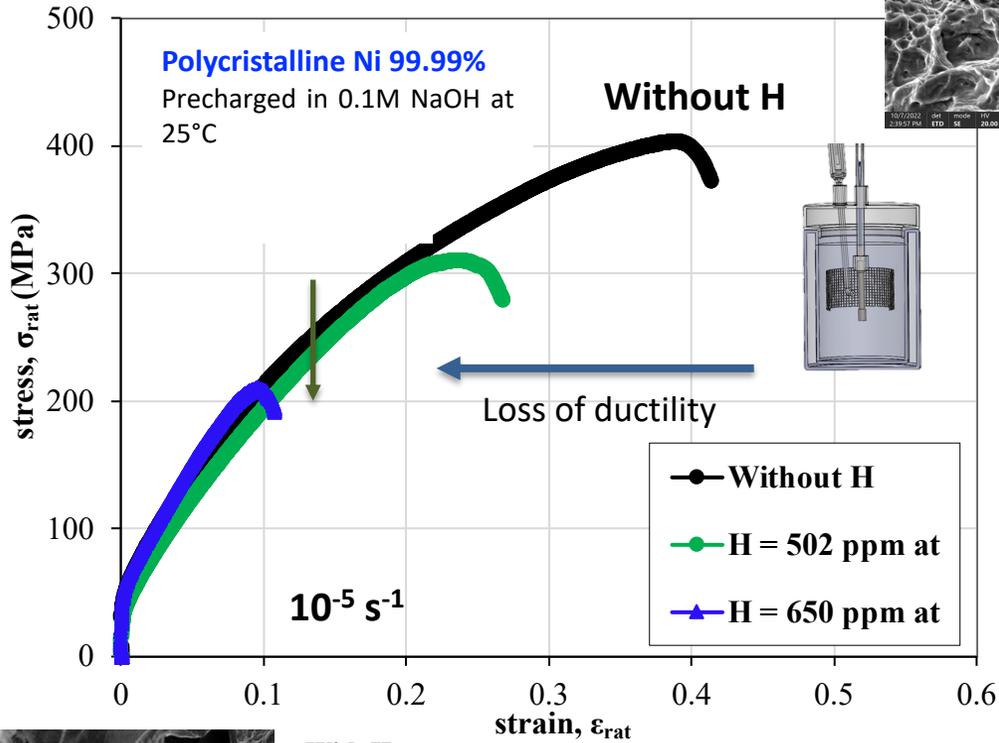
Y. Ben Jedidia, S. P. Murugan, N. Iskounen, A. Radi, J. Li, C. Traisnel



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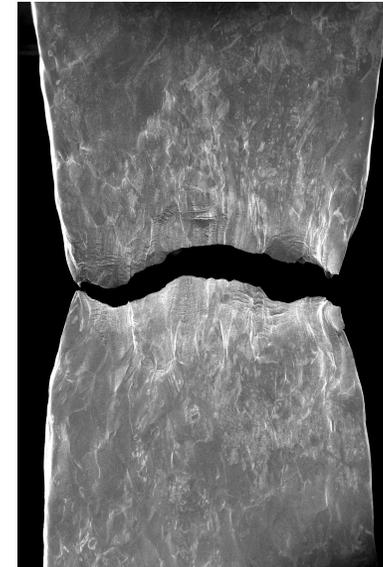


## Consequences of H on mechanical behaviour

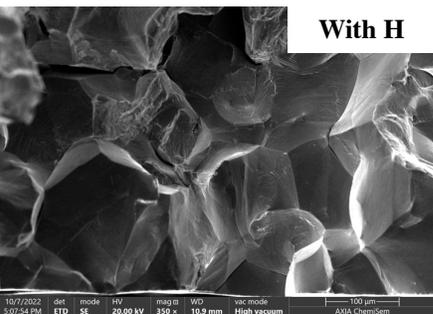
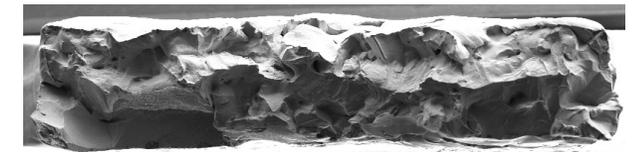
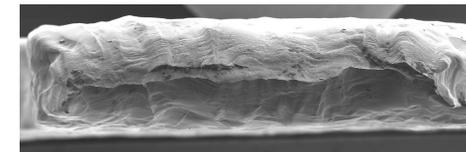
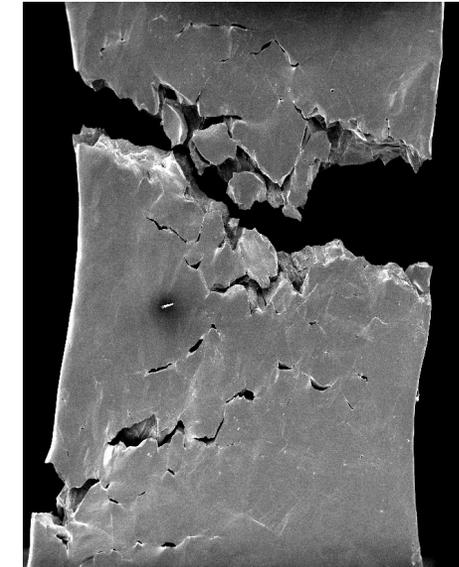


Concretely!

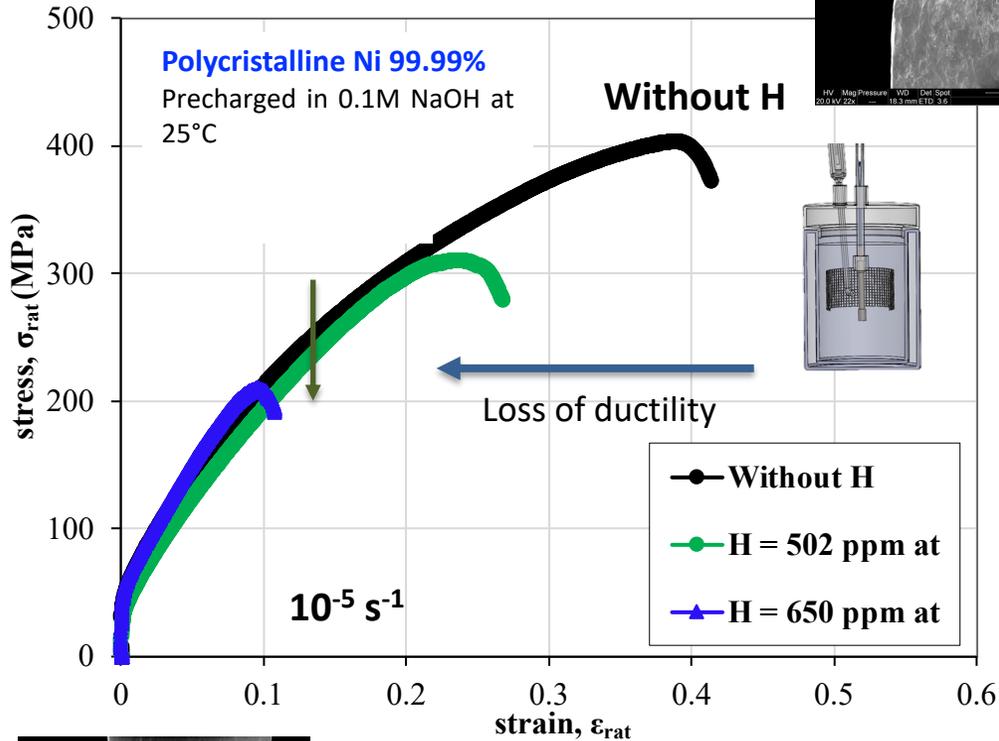
Without H



With H



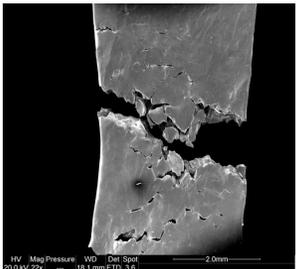
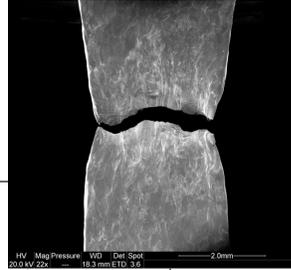
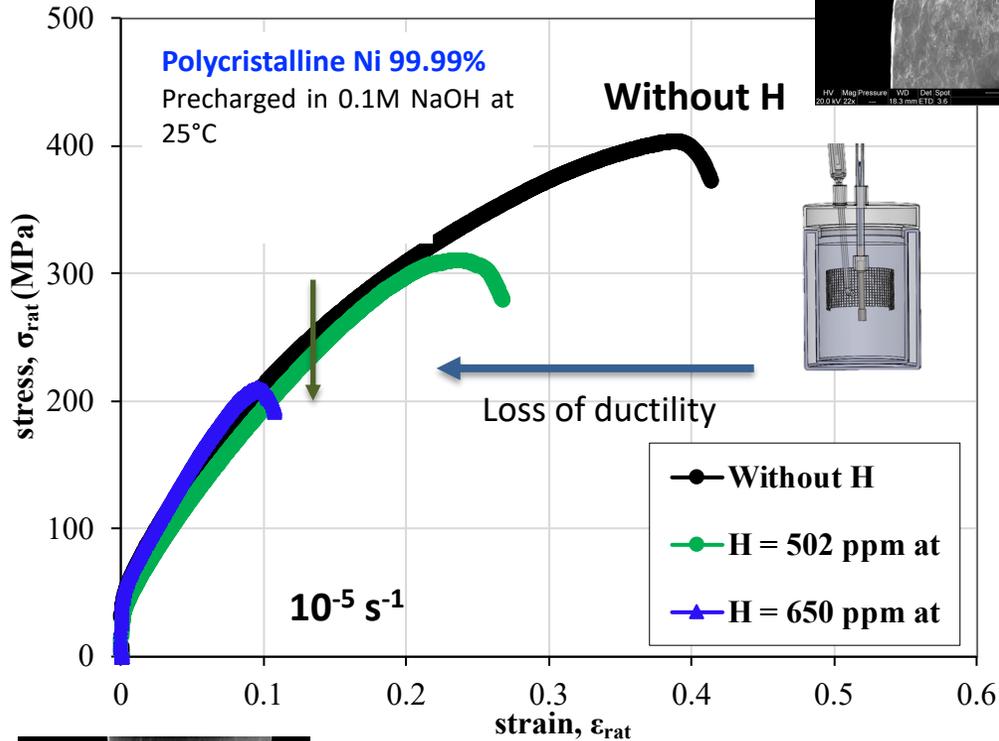
## Consequences of H on mechanical behaviour



## Some Models of Hydrogen Embrittlement

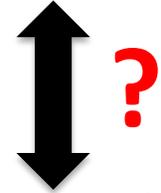
- Hydrogen-enhanced decohesion (HEDE)**: lowering of the cohesive energy of interfaces due to hydrogen segregation [Oriani, Corrosion 1987; Gerberich *et al.* Hydrogen effects in Materials 1996]
- Hydrogen-enhanced localized plasticity (HELP)**: reduction of the interaction energy between dislocations and obstacles promoting slip localization [Robertston *et al.* Dislocations in Solids 2009; Nagao *et al.* Encyclopedia of iron, steel and their alloys 2016]
- Super-abundant vacancies (SAV)**: enhancement of vacancies formation by hydrogen [Nagumo M., Mater Sci technol 2004]

## Consequences of H on mechanical behavior



## Some Models of Hydrogen Embrittlement

- Hydrogen-enhanced decohesion (HEDE)
- Hydrogen-enhanced localized plasticity (HELP)
- Super-abundant vacancies (SAV)



## The implication of Hydrogen-Defects interactions?

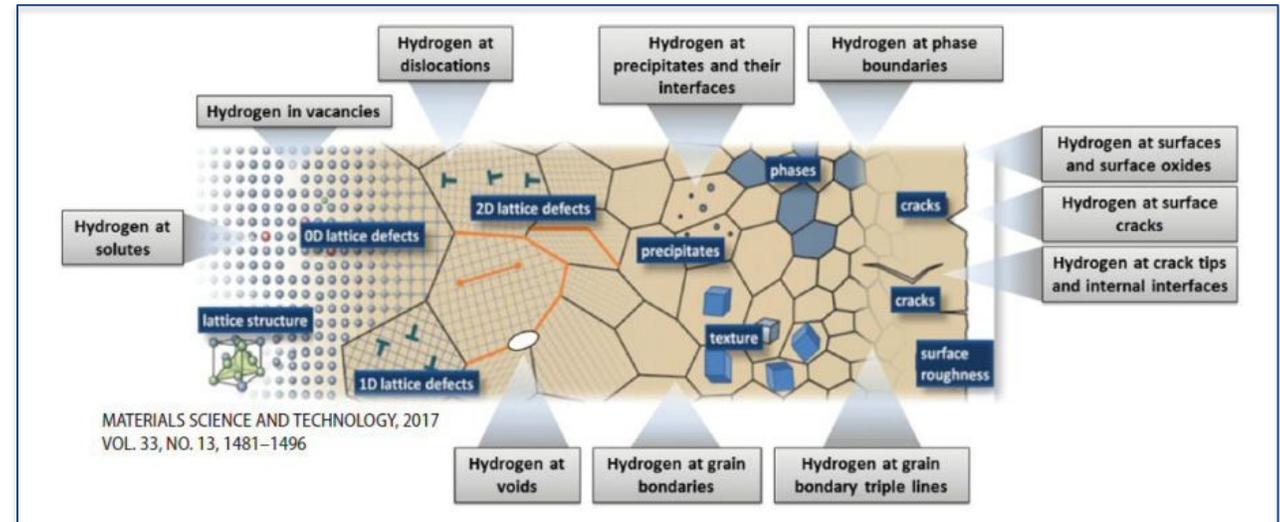
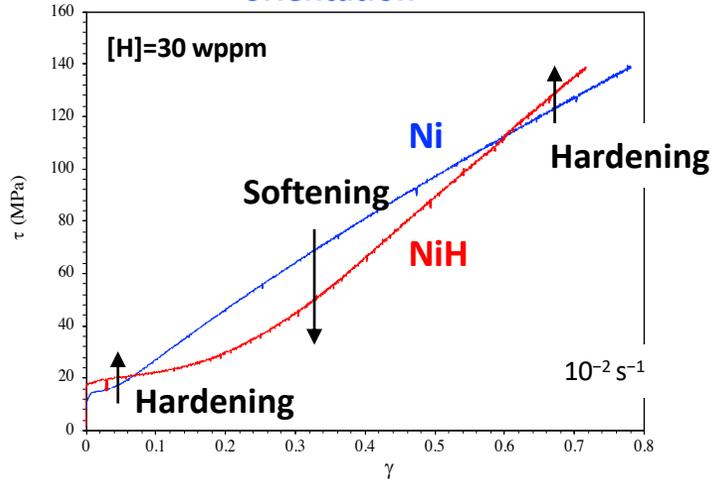
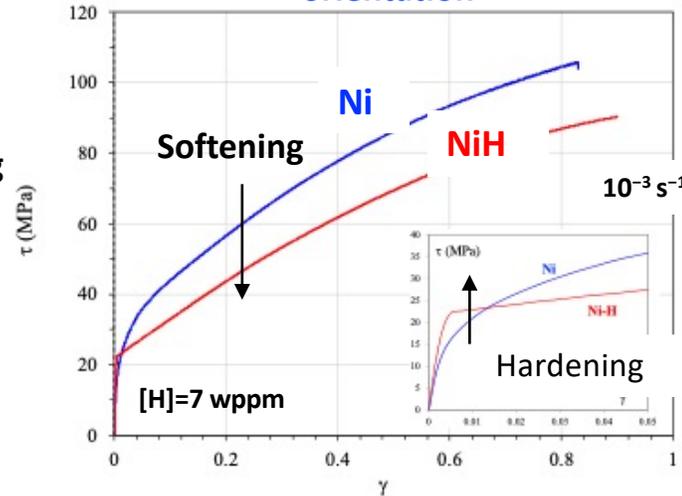


Illustration of several possible hydrogen sites. Hydrogen embrittlement is dependent on hydrogen trapping and kinetics related to microstructural sensitivity.

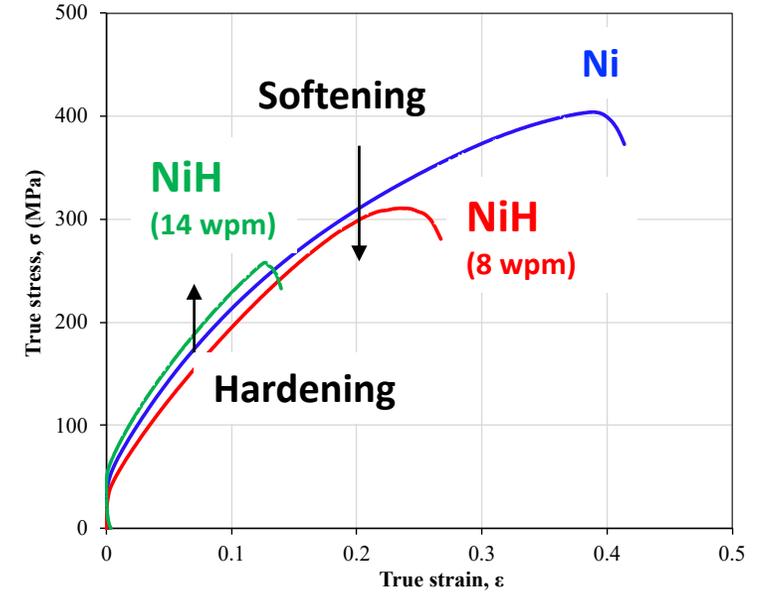
Tensile Stress-Strain Curves of Ni [135] orientation<sup>[1]</sup>



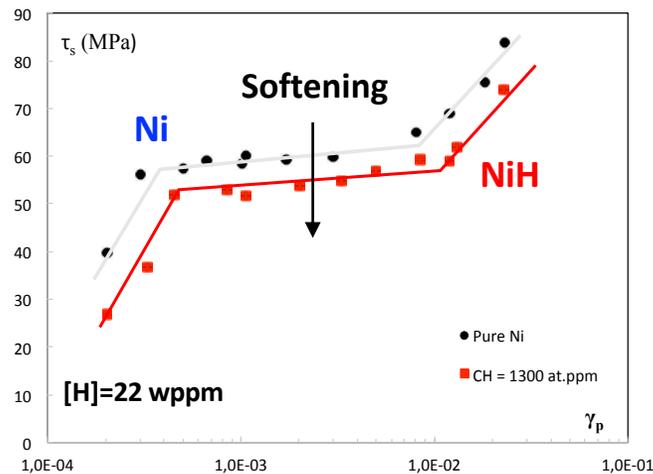
Tensile Stress-Strain Curves of Ni [001] orientation<sup>[3]</sup>



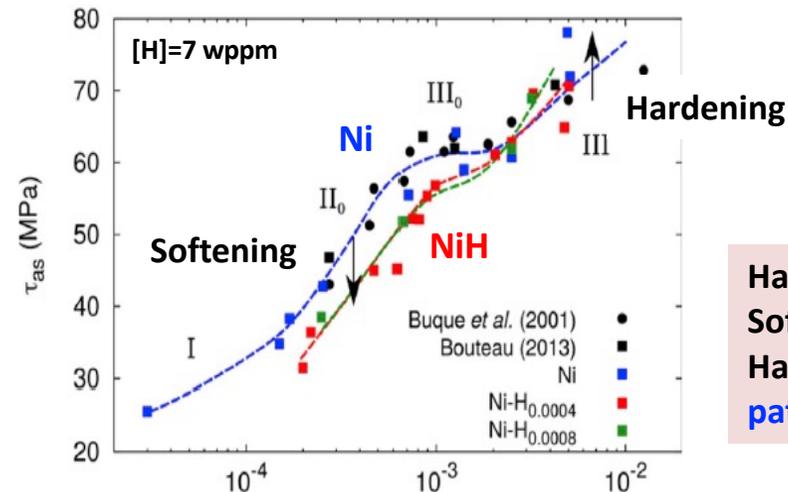
Tensile Stress-Strain Curves of polycrystalline Ni (150 μm)<sup>[5]</sup>



Cyclic stress-strain curve of Ni<135> <sup>[2]</sup>



Cyclic stress-strain curve of Ni<001> <sup>[4]</sup>



**Hardening:** Increase of the drag stress by Cottrell atmosphere  
**Softening:** Shielding effect of H and delay of cross-slip events  
**Hardening:** Reduction of interwall distances and dislocation length path

[1] G. Girardin, C. Huvier, D. Delafosse, X. Feugas; *Acta Materialia* 91 (2015) 141-151.

[2] T. Magnin, C. Bosch, K. Wolski, D. Delafosse; *Materials Science and Engineering A314* (2001) 7-11.

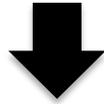
[3] E. Ghermaoui et al. *Scientific Reports* 9 (2019) 13042.

[4] G. Hachet et al. *International Journal of Plasticity* 126 (2020) 102611.

[5] PhD of Y. Ben Jedidia 2024

❑ Intergranular fracture?

❑ Softening and hardening effects?

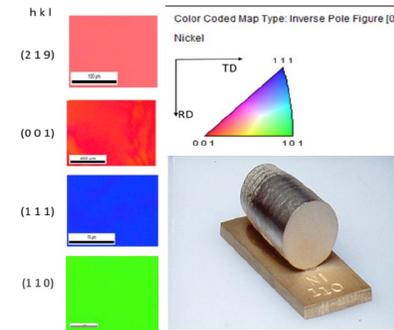


- ✓ Context and motivations
- ✓ Hydrogen vs. Grain Boundary Character
- ✓ Hydrogen vs. Vacancies vs. Dislocations
- ✓ Hydrogen vs. Precipitates
- ✓ Main results and perspectives

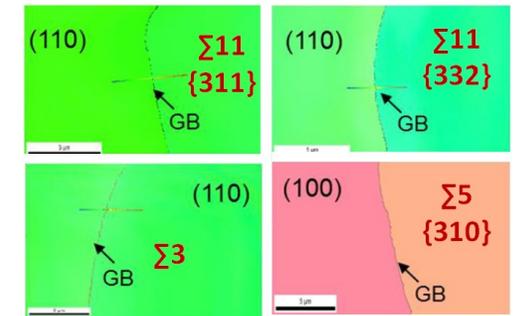
## Nickel and Nickel base alloys

### The microstructures

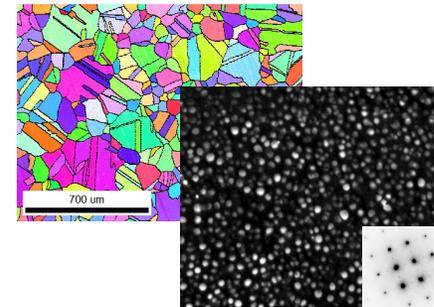
#### Single crystals



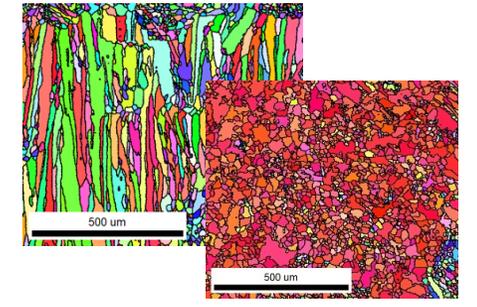
#### Bicrystals



#### Waspaloy - Precipitates

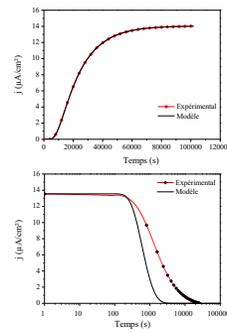


#### IN 718 AM – Complex!



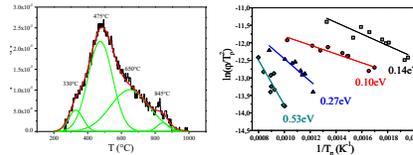
## Quantification and diffusion of hydrogen

### Electrochemical permeation (EP)



Evaluation of hydrogen diffusion coefficients in a membrane, concentrations of diffusible and trapped hydrogen ...

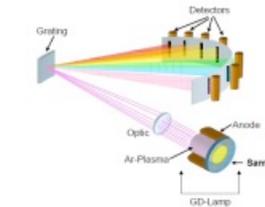
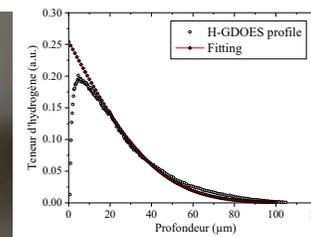
### Thermal Desorption (TDS)



Measurement of hydrogen concentrations, identification of hydrogen states ...

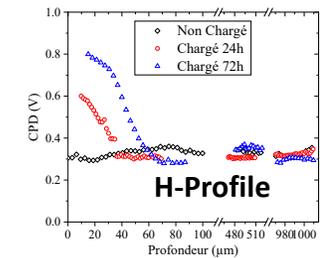
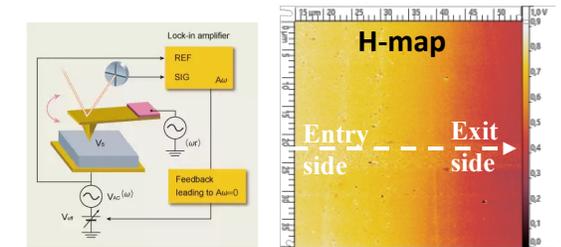
## Mapping and distribution of hydrogen

### Glow Discharge Optical Emission Spectrometry (GD-OES)



Measurement of hydrogen profile  
Placamat - Bordeaux

### Scanning Kelvin Probe Force Microscopy (SKPFM)



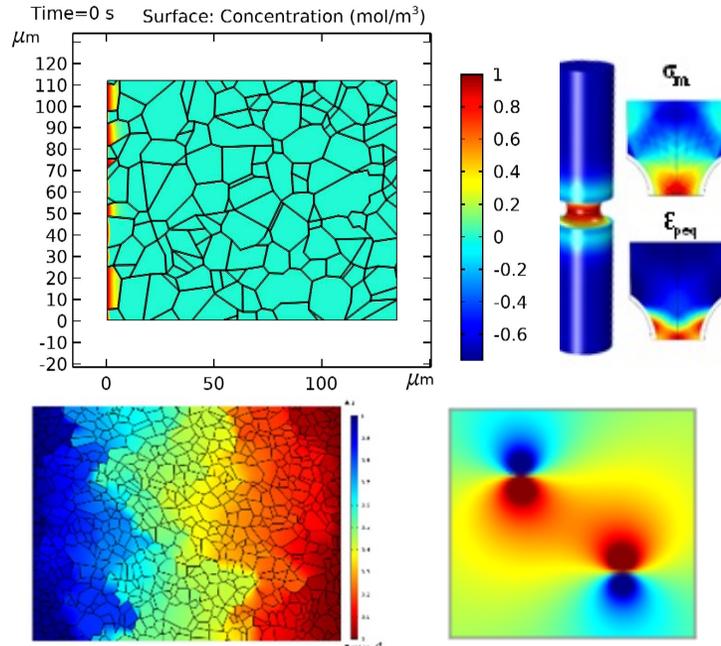
Hydrogen localization and profile

M. Duportail et al. Scripta Mater. (2020)

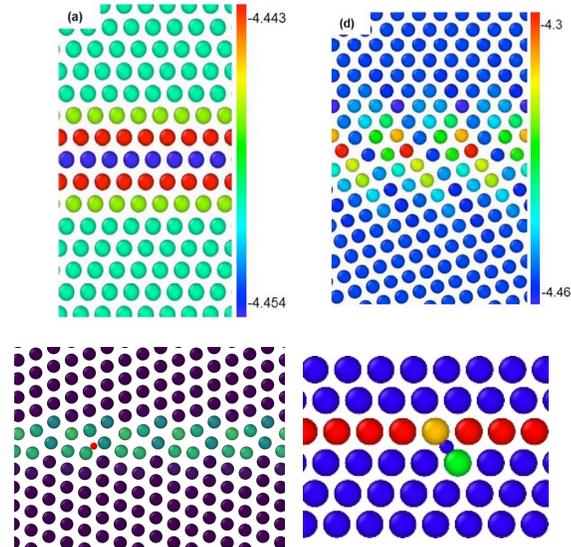


With: J. Bouhattate, A. Metsue, M. Landeiro dos Reis, A. Hallil, N. Iskounoun,

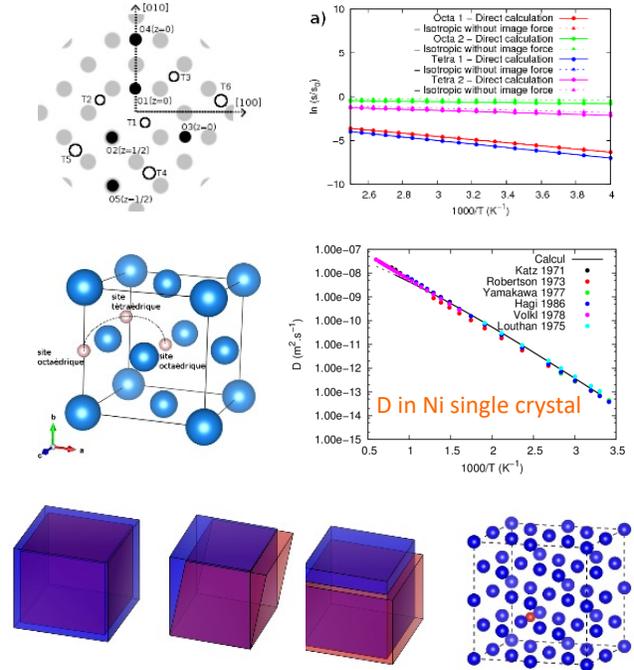
## Finite Element Method Calculations (FEM)



## Atomistic calculations (LAMMPS)



## Calculations by Density Functional Theory (DFT) and ab-initio

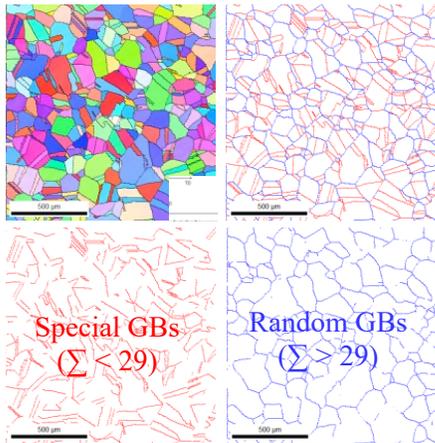


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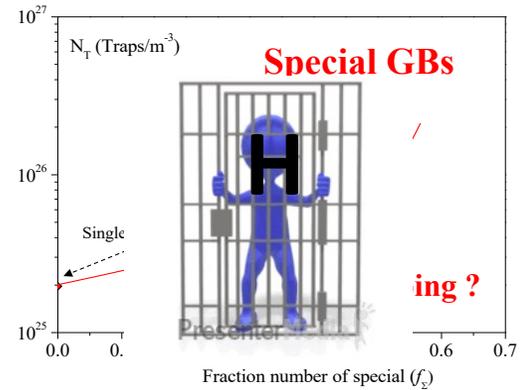
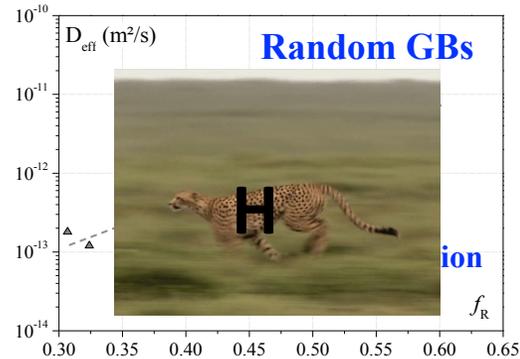
*Intergranular fracture vs. GBs character*

## A consequence of grain size evolution on H diffusion and trapping

Polycrystalline nickel  
Grain size from 50 nm to 168 μm



A. Oudriss, *et al.*, Acta Mater., 2012

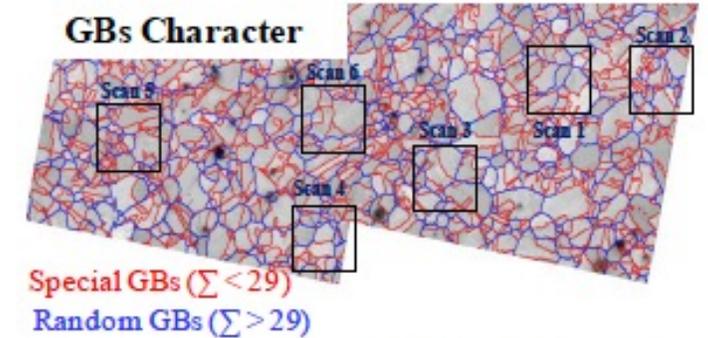
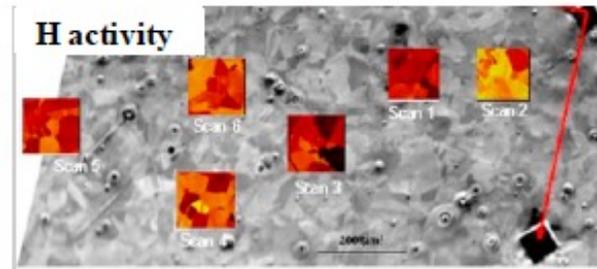


## Tof-SIMS and EBSD analyses on precharged H polycrystalline Ni

Polycrystalline nickel

(18 μm/45 μm, C<sub>H</sub>=15 wppm, aged 2-3 weeks)

Number of grains boundaries analyzed: 100/character

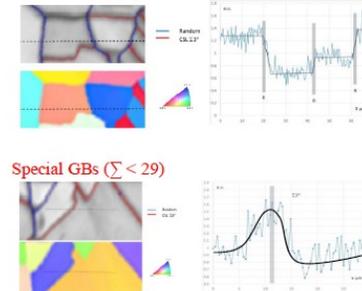


Nature of GBs

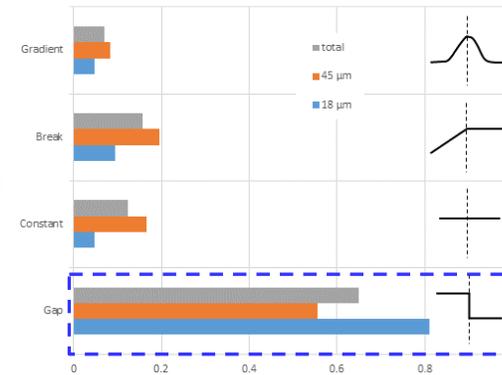
Random GBs (Σ > 29)

Special GBs (Σ < 29)

H concentration profil

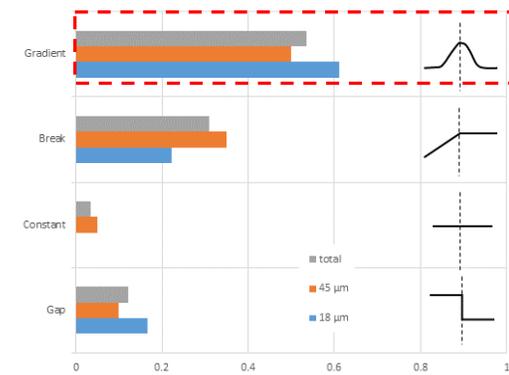


Random GBs (Σ > 29)



Gap of H concentration  
→ Diffusion along Random GBs ?

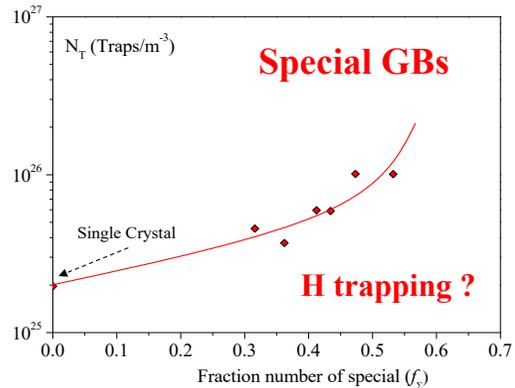
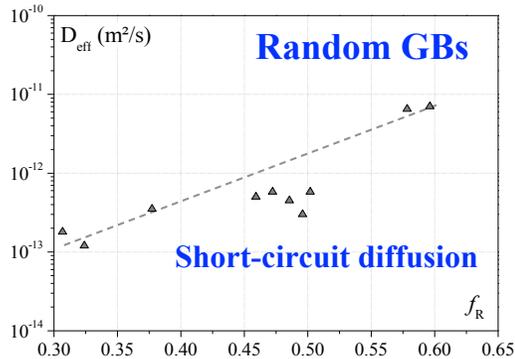
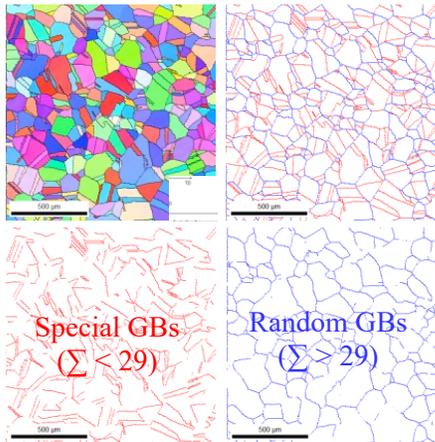
Special GBs (Σ < 29)



Gradient of H concentration  
→ Trapping by Special GBs?

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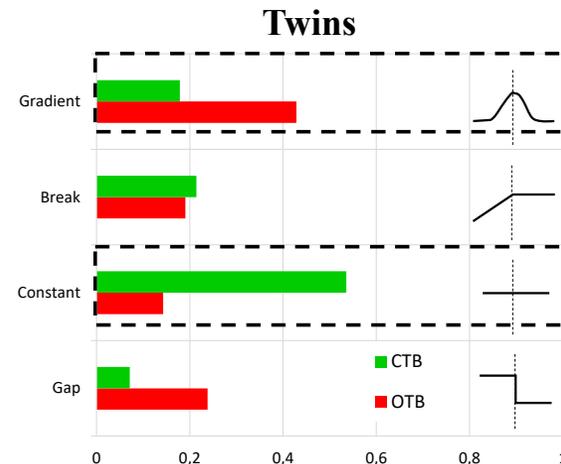
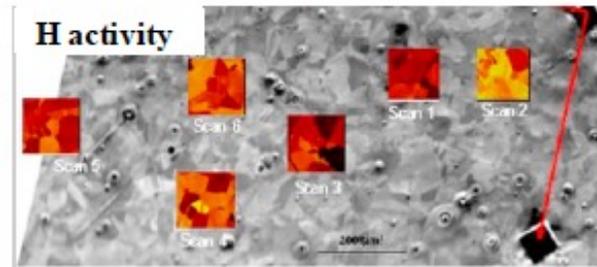
A. Oudriss, *et al.*, Acta Mater., 2012

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(18 μm/45 μm, C<sub>H</sub>=15 wppm, aged 2-3 weeks)

Number of grains boundaries analyzed: 100/character



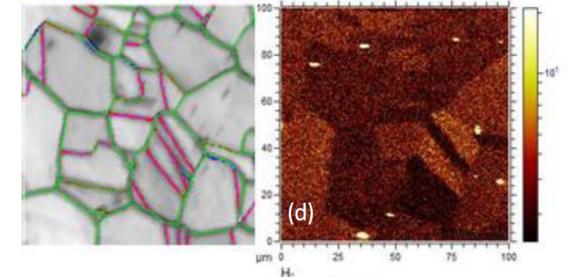
CTB → No effect ?

OTB → Trapping ?

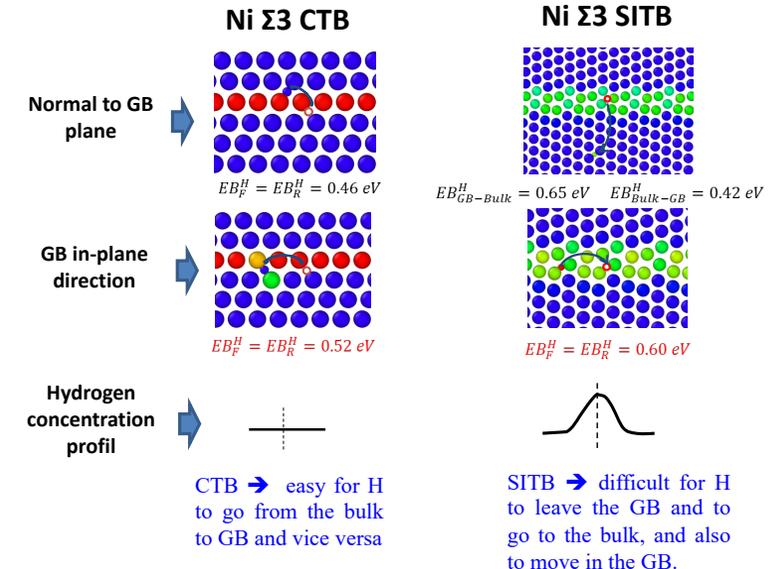


Twins

H



Atomistic calculations  
(LAMMPS) by A. Hallil

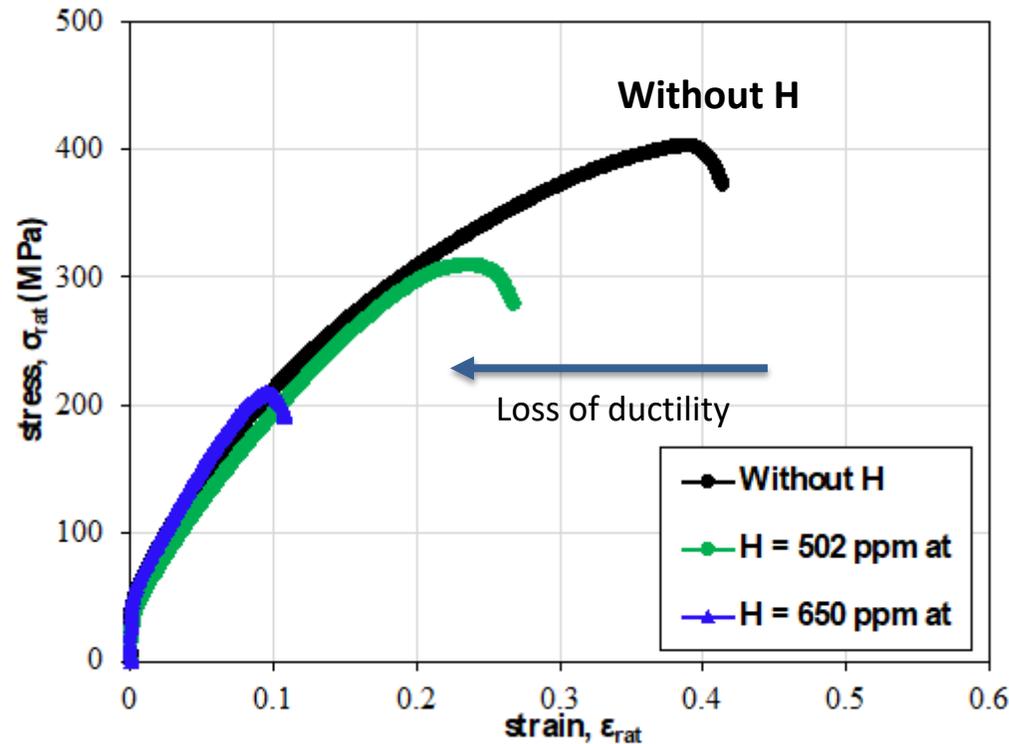


CTB → easy for H to go from the bulk to GB and vice versa

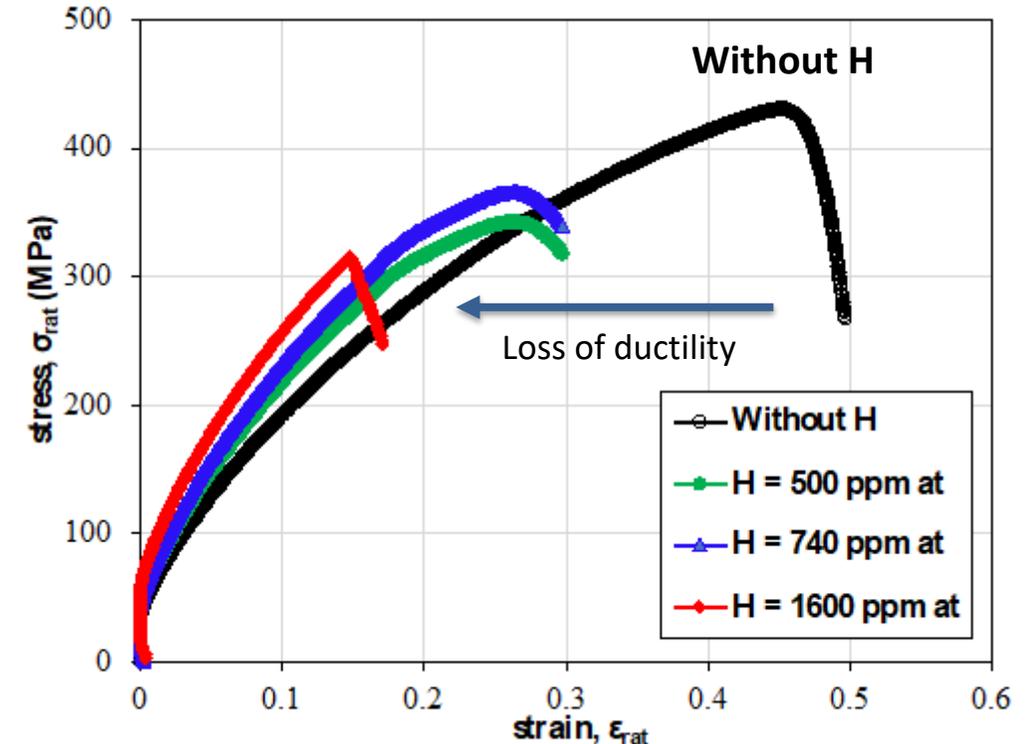
SITB → difficult for H to leave the GB and to go to the bulk, and also to move in the GB.

✓ Wavy slip (easy cross-slip) – intergranular fracture *versus*  $C_H$

Special GBs ( $\Sigma 1$ - $\Sigma 29$ ) = 60-65%



Special GBs ( $\Sigma 1$ - $\Sigma 29$ ) = 70-75%



- Fracture modes? → Fractography analysis
- Impact of Hydrogen and GBs character on the elongation ratio ?

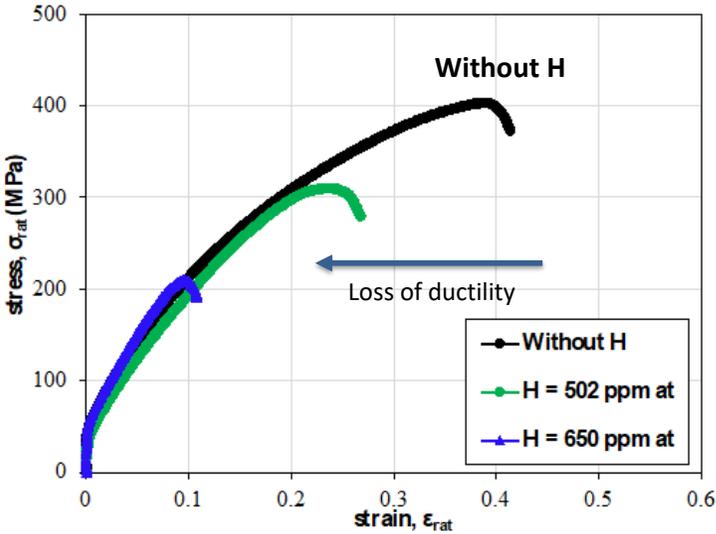
PhD Y. Ben Jedia (2021-2024)

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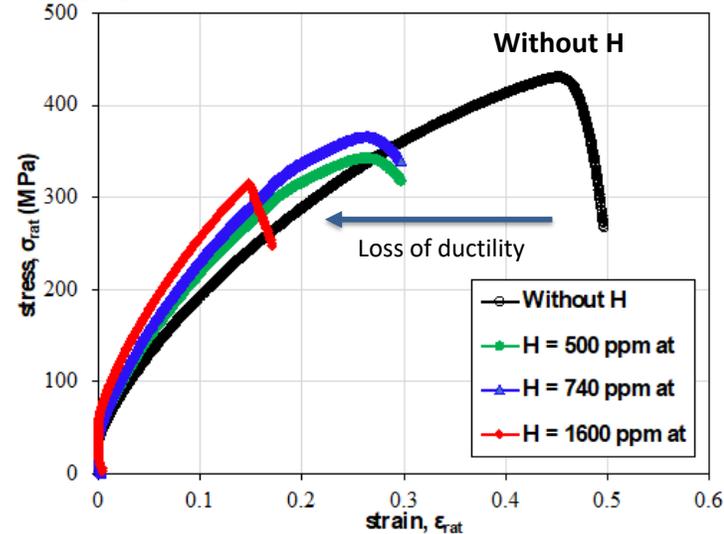
### Polycrystalline Ni



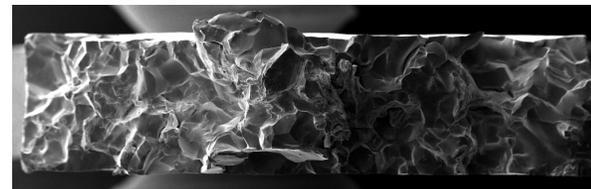
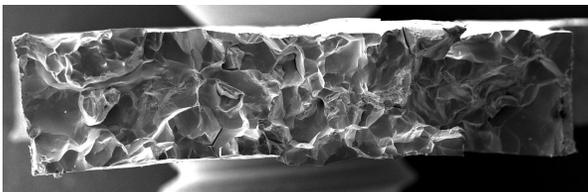
CSL ( $\Sigma 1$ - $\Sigma 29$ ) = 60-65%



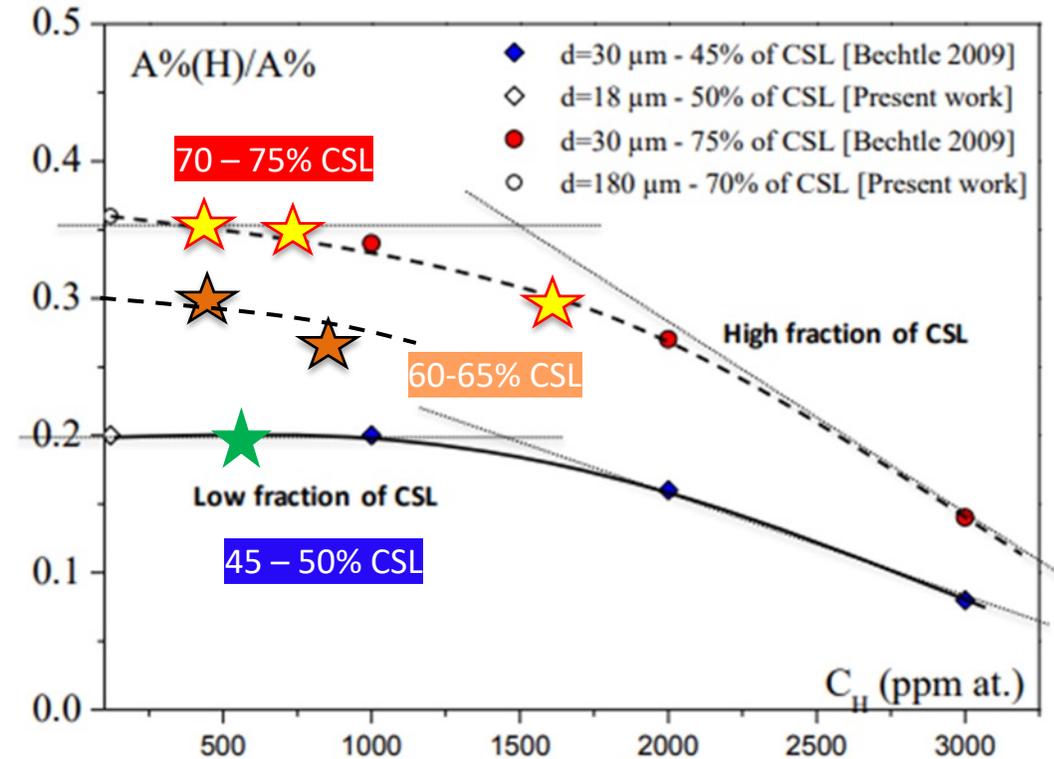
CSL ( $\Sigma 1$ - $\Sigma 29$ ) = 70-75%



Intergranular fracture



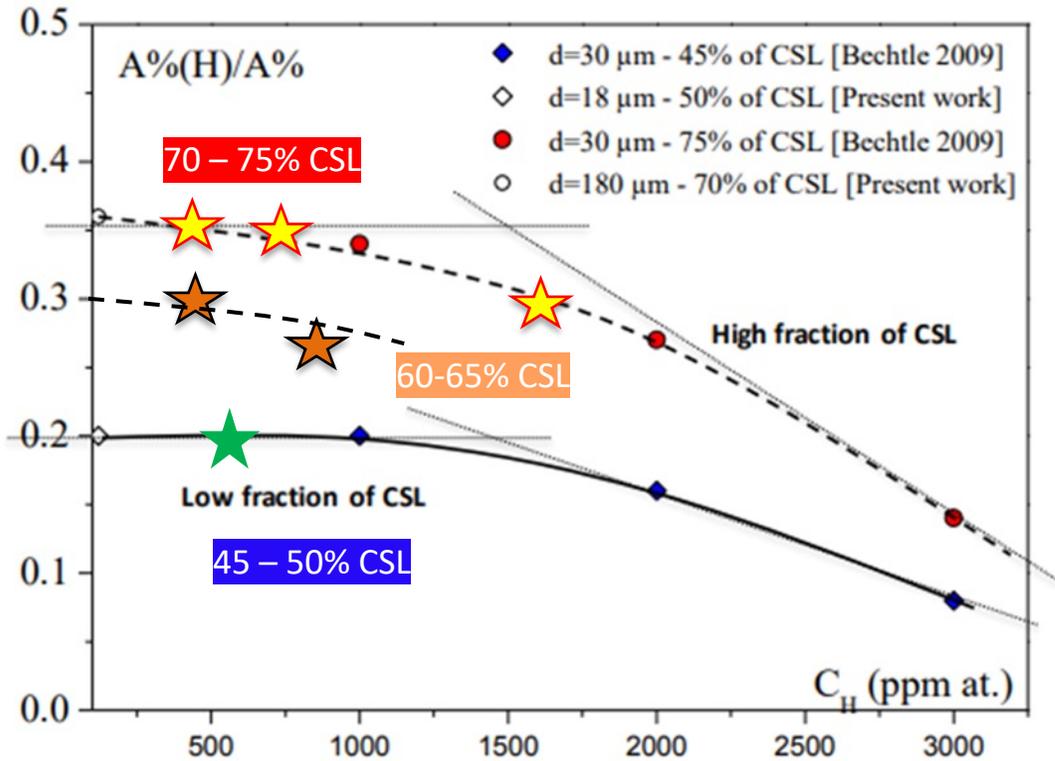
### Elongation ratio



In progress...

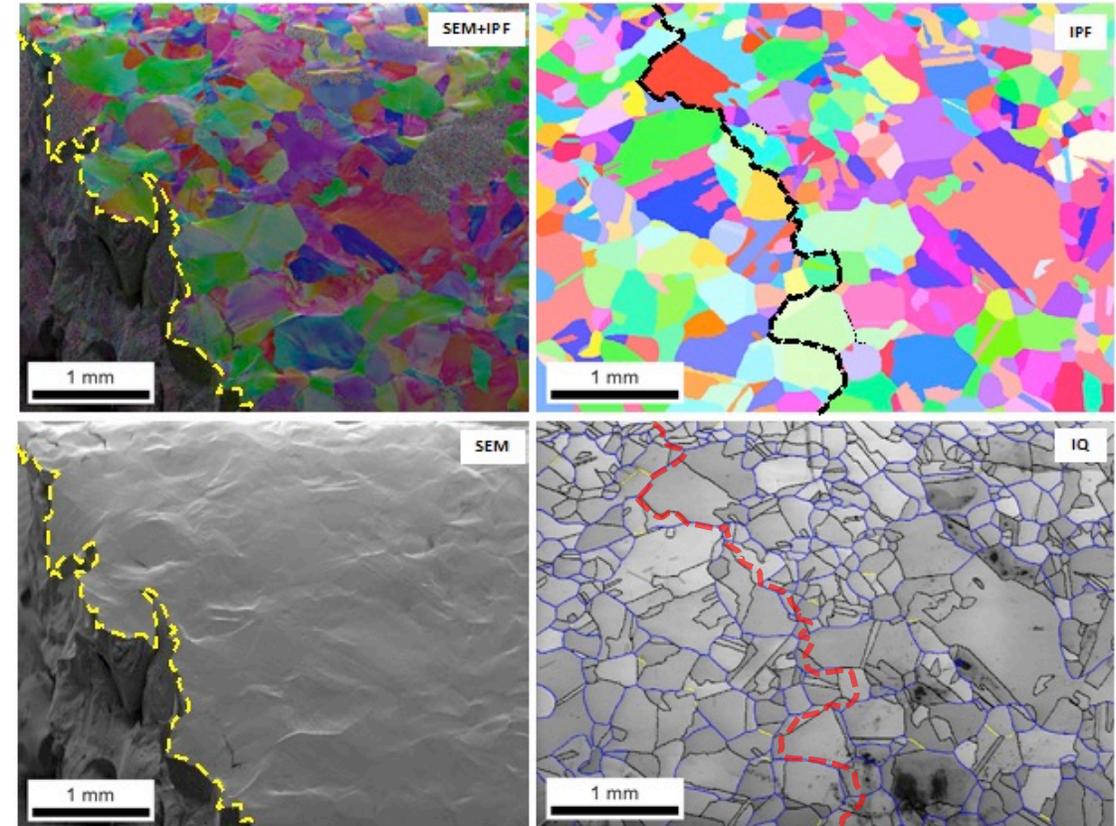
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### Elongation ratio



✓ Preferential intergranular fracture along Random GB

### Preferential intergranular propagation



— CSL    — LAGB    — RANDOM

In progress...

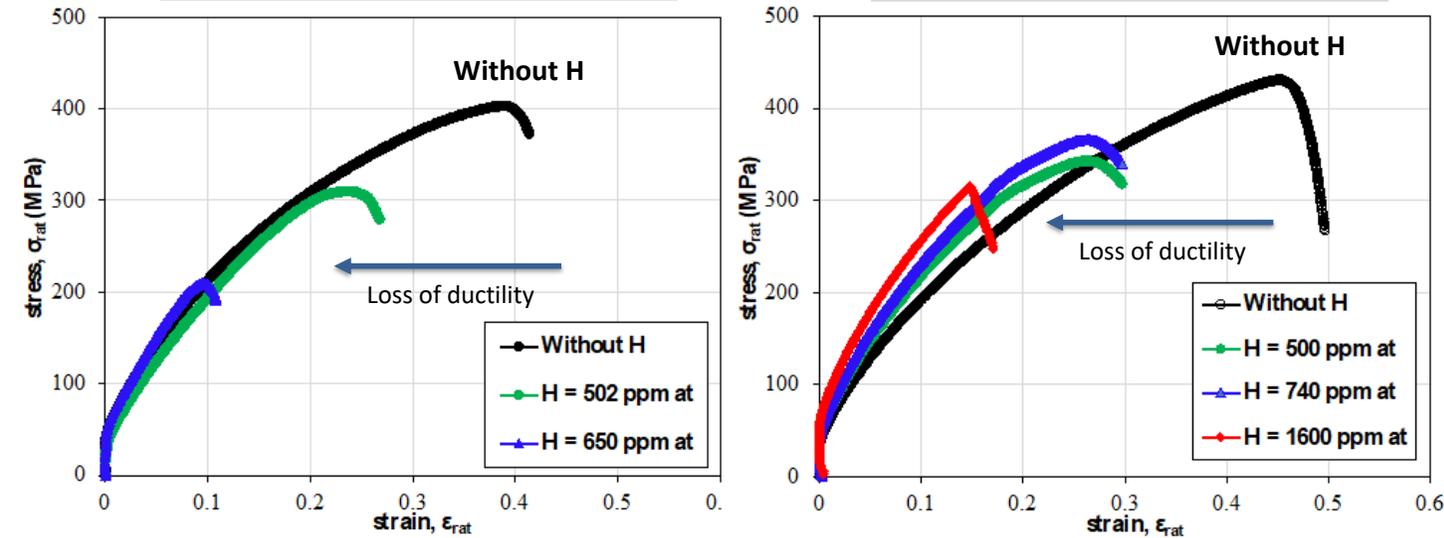
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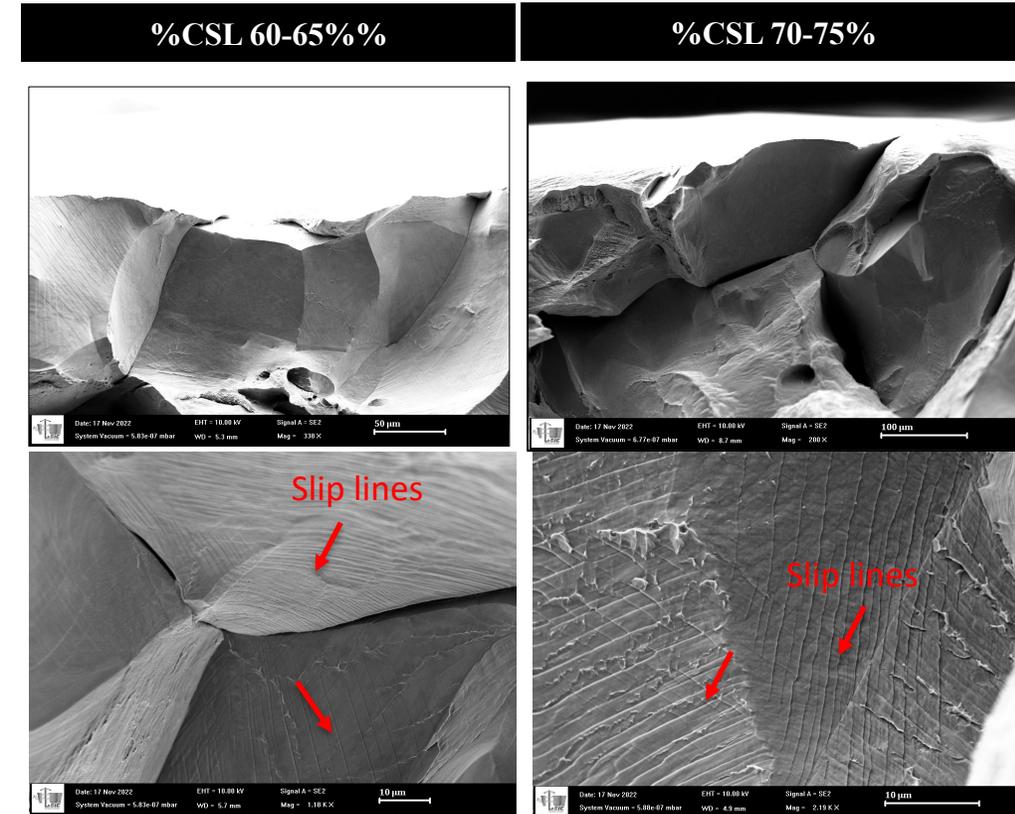
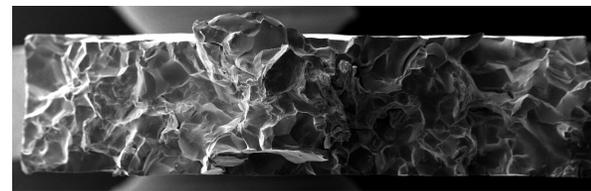
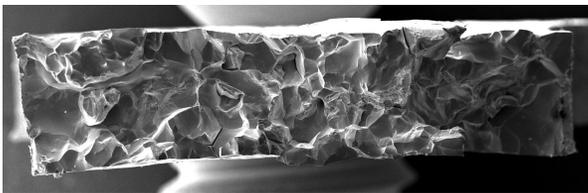
### Polycrystalline Ni

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CSL ( $\Sigma 1$ - $\Sigma 29$ ) = 70-75%



Intergranular fracture



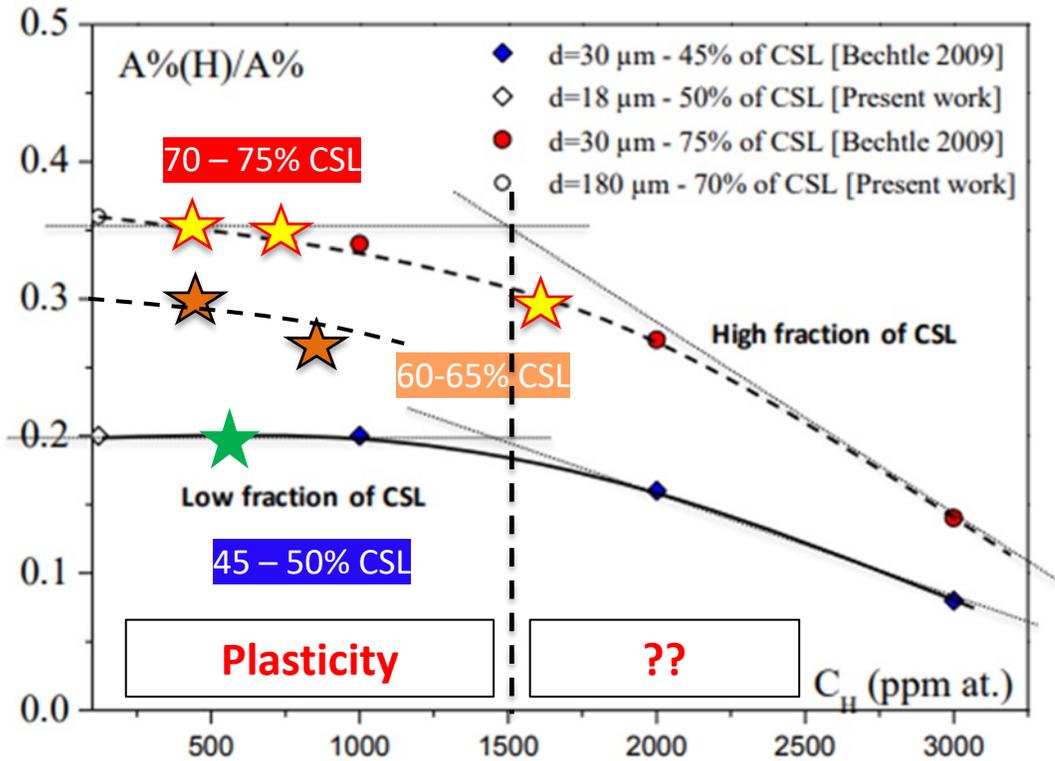
Slip lines

**Contribution of the plasticity on the intergranular fracture**

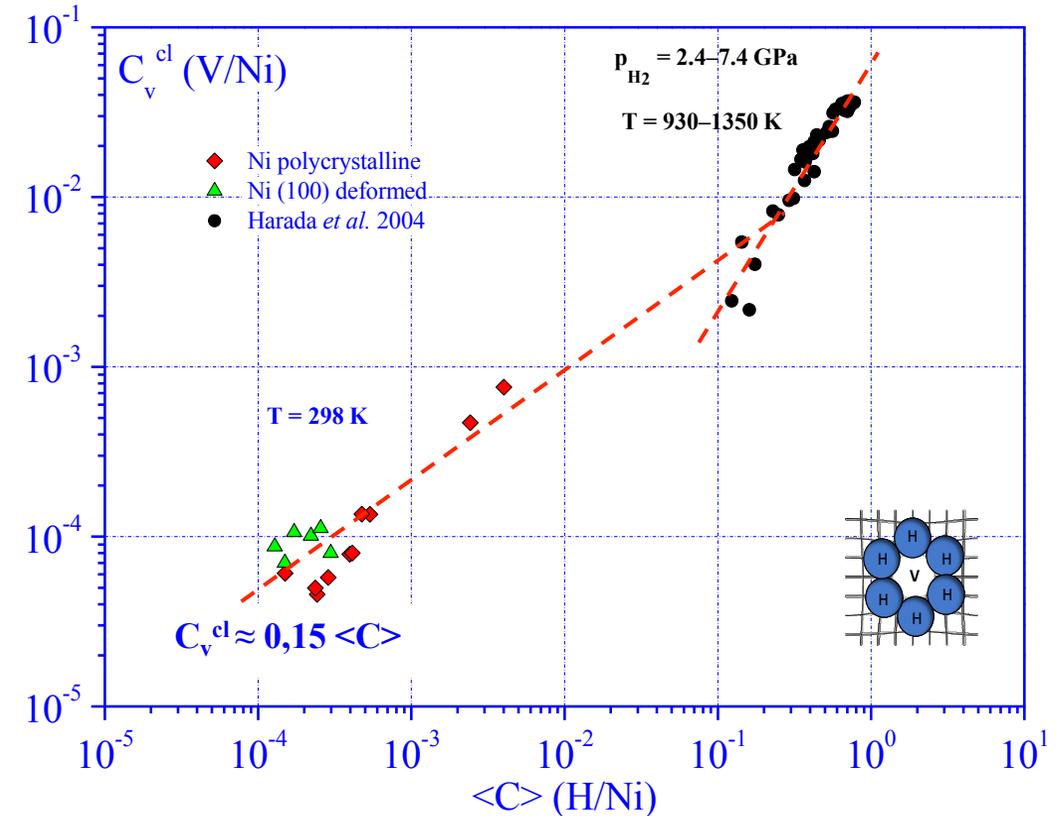
✓ Wavy slip (easy cross-slip) – intergranular fracture *versus*  $C_H$

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### Elongation ratio



### Hydrogen promotes formation of vacancies

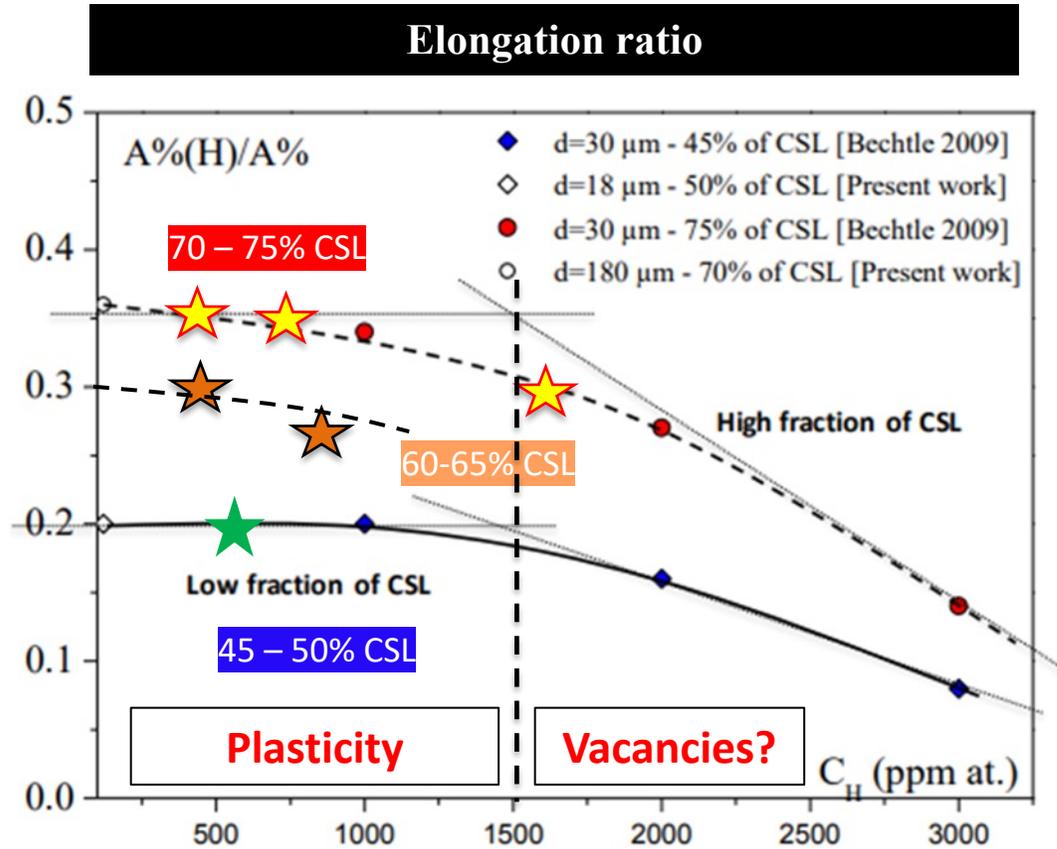


- ✓ At high concentrations of H => Loss of resistant of Special GBs to HE
- ✓ Hydrogen favor the formation of new vacancies (S.A.V)?

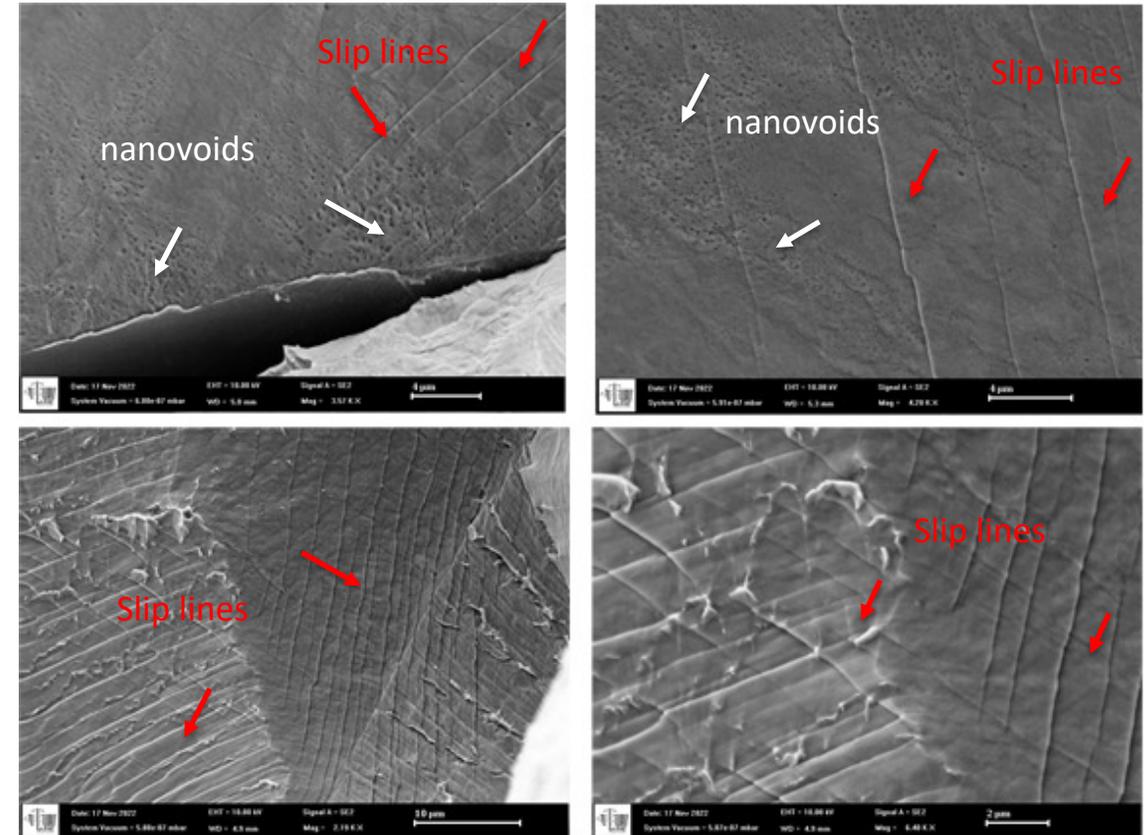
A. Oudriss *et al.*, Acta Mater., 2012  
 A. Oudriss *et al.*, Acta Mater., 2023

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### Presence of nanovoids and slip lines

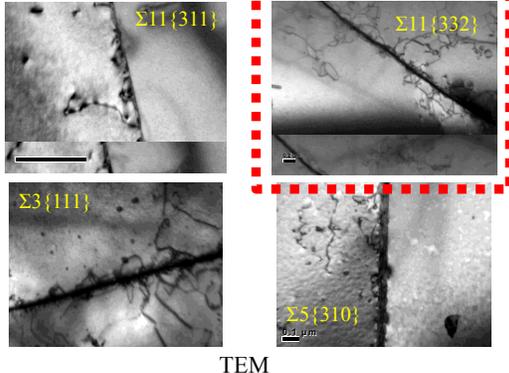
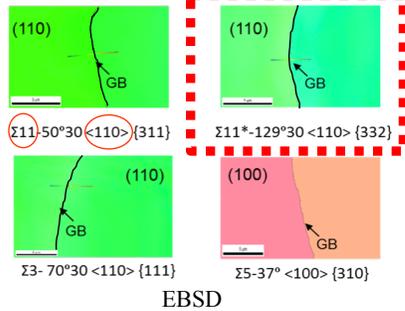


✓ At high concentrations of H => Loss of resistant of Special GBs to HE  
 ✓ Hydrogen favor the formation of new vacancies (S.A.V)?

**Contribution of plasticity and vacancies (nano-cavities)!**

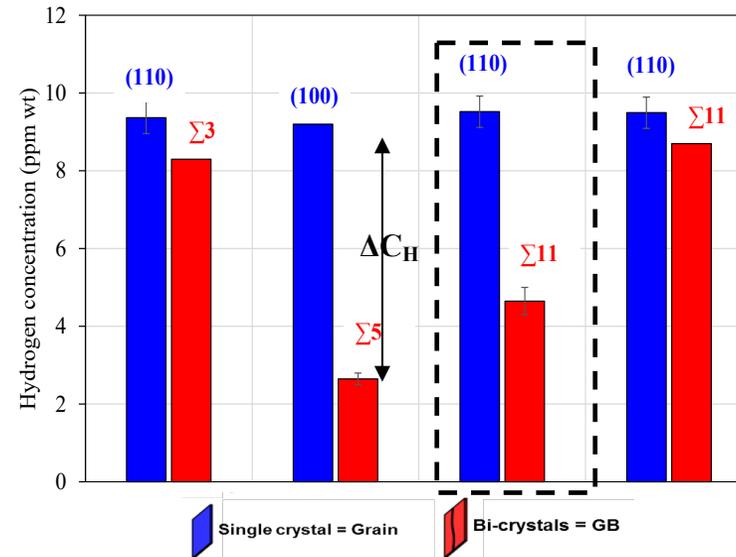
## Bicrystals : identification of GB

Bi crystals Provided by L. Priester (ICMPE) and Ecole des Mines de Saint-Etienne (ENSM-SE)

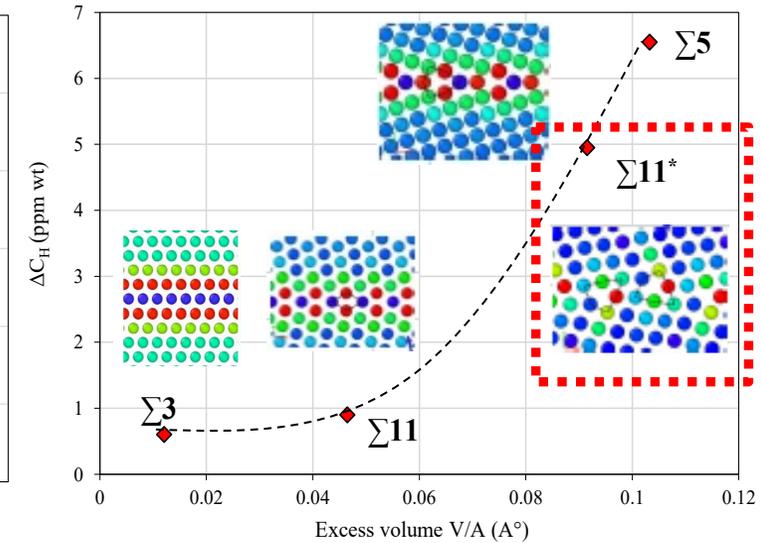


- ~~$\Sigma 3$  CTB~~
- ~~$\Sigma 5$  37° <100> {310}~~
- $\Sigma 11^*$  129° <110> {332}
- ~~$\Sigma 11$  50° <110> {311}~~

## H-concentration by TDS



## Hydrogen and excess volume (GB energy)

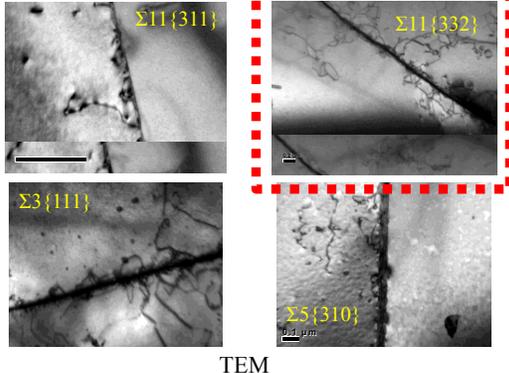
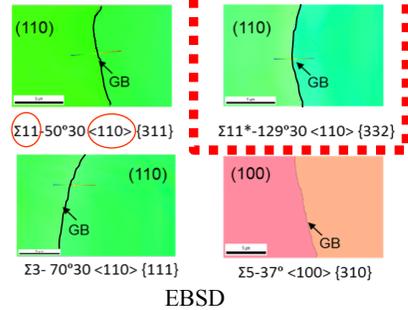


In situ tensile tests

In progress...

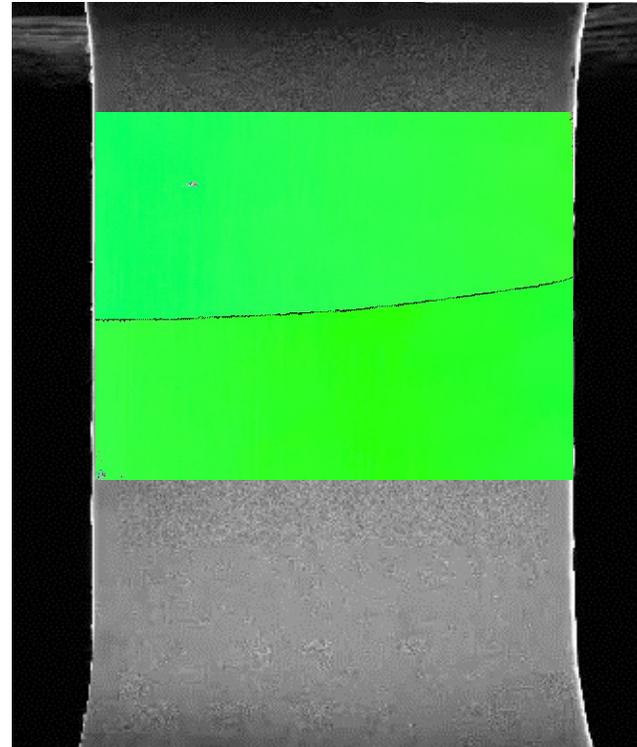
## Bicrystals : identification of GB

Bi crystals Provided by L. Priester (ICMPE) and Ecole des Mines de Saint-Etienne (ENSM-SE)

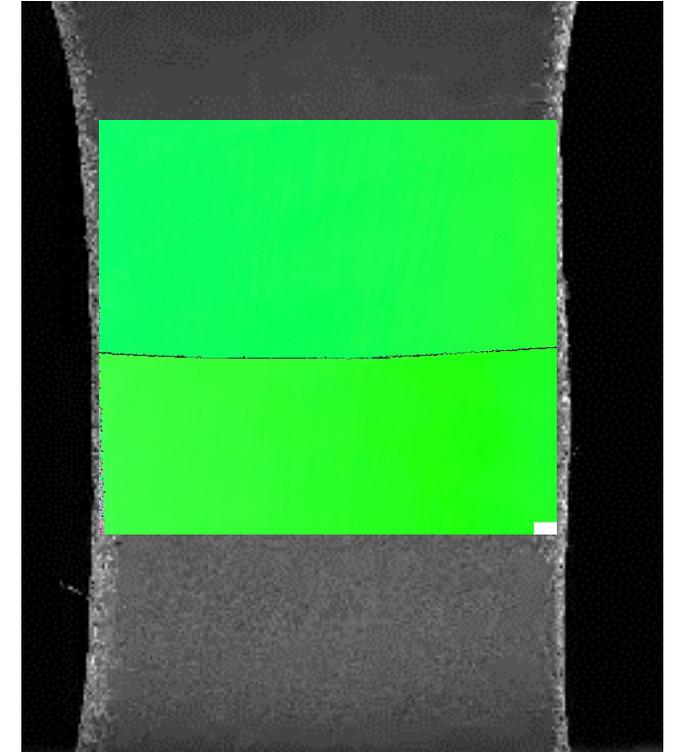


- ~~$\Sigma 3$  CTB~~
- ~~$\Sigma 5$   $37^\circ \langle 100 \rangle \{310\}$~~
- $\Sigma 11^*$   $129^\circ \langle 110 \rangle \{332\}$
- ~~$\Sigma 11$   $50^\circ \langle 110 \rangle \{311\}$~~

## Without H



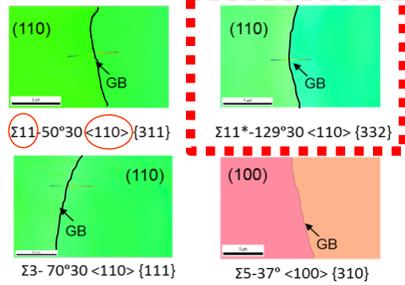
## With H



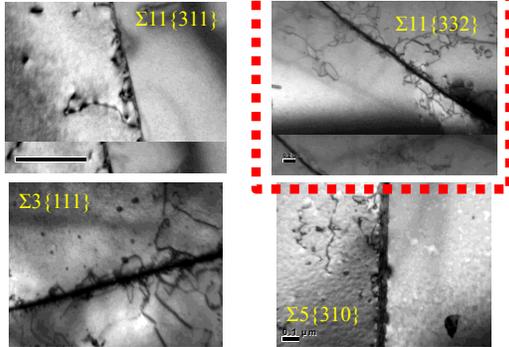
In progress...

### Bicrystals : identification of GB

Bi crystals Provided by L. Priester (ICMPE) and Ecole des Mines de Saint-Etienne (ENSM-SE)



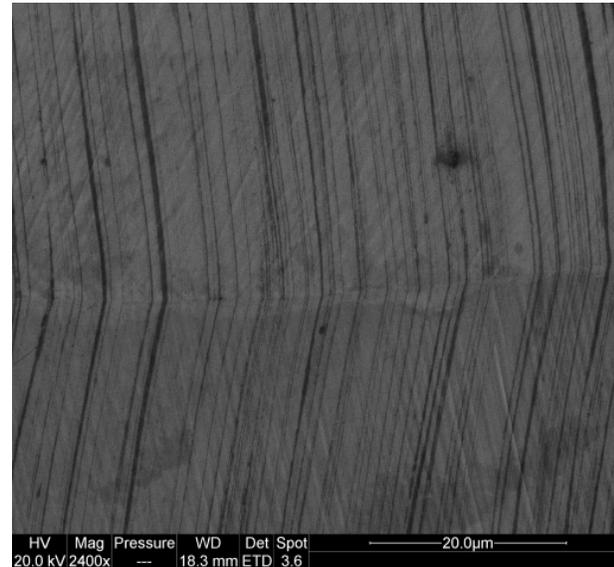
EBSD



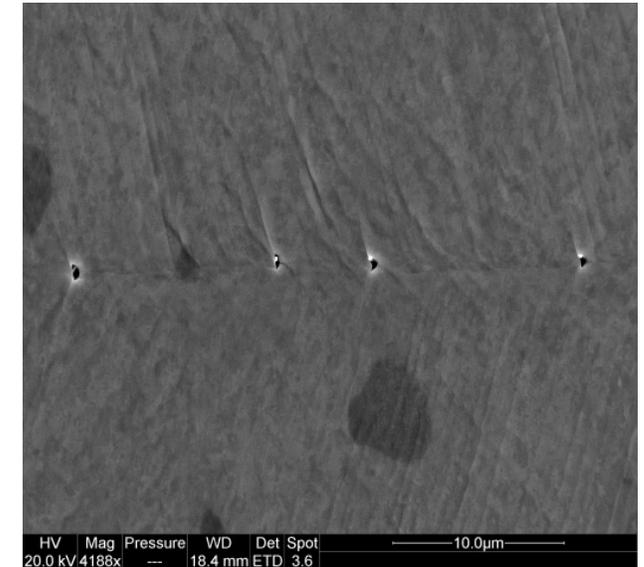
TEM

- ~~Σ3 CTB~~
- ~~Σ5 37° <100> {310}~~
- **Σ11\* 129° <110> {332}**
- ~~Σ11 50° <110> {311}~~

### Without H



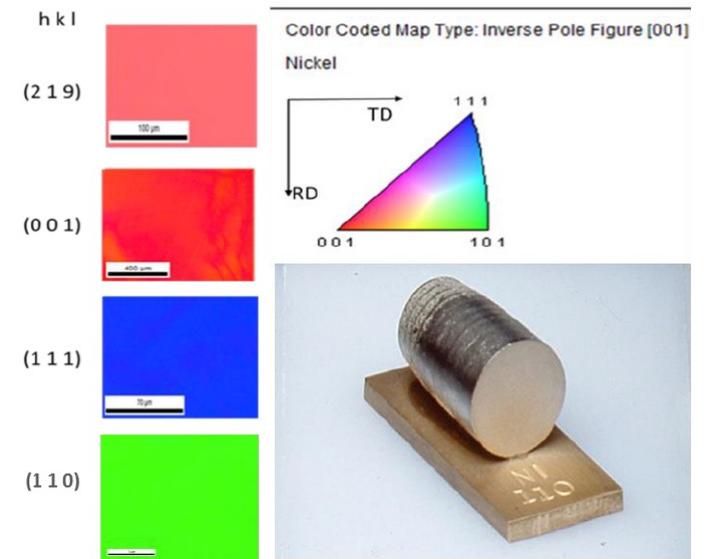
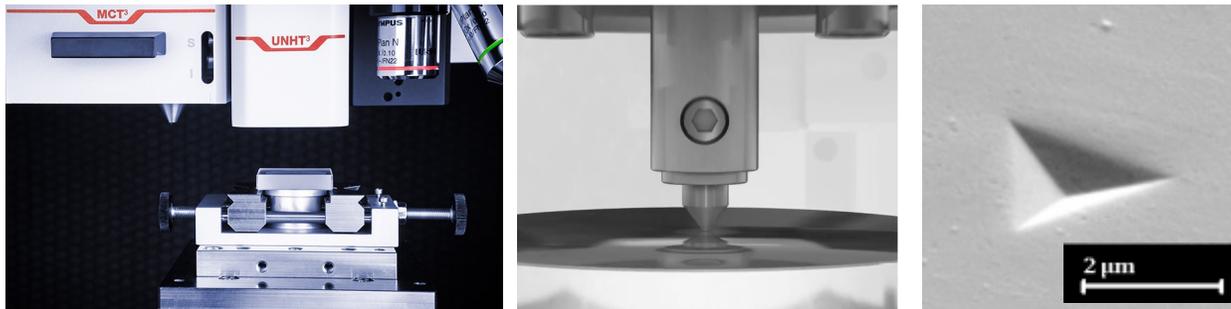
### With H

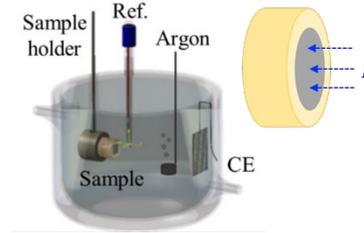
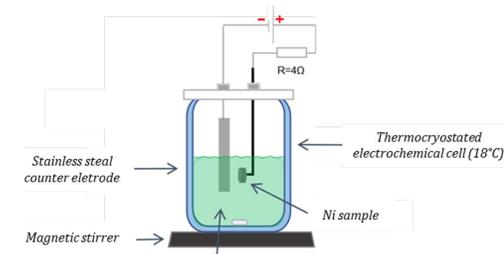


In progress...

# Hydrogen vs. Vacancies vs. Dislocations

## The nanoindentation



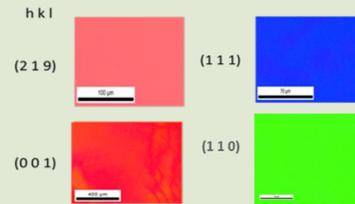


- Current density: 260 mA/cm<sup>2</sup>
- Duration: 10 min
- Rotation speed: 350 rpm
- Temperature: 18°C

### Electropolishing

### EBSD

- Identification of grains orientations



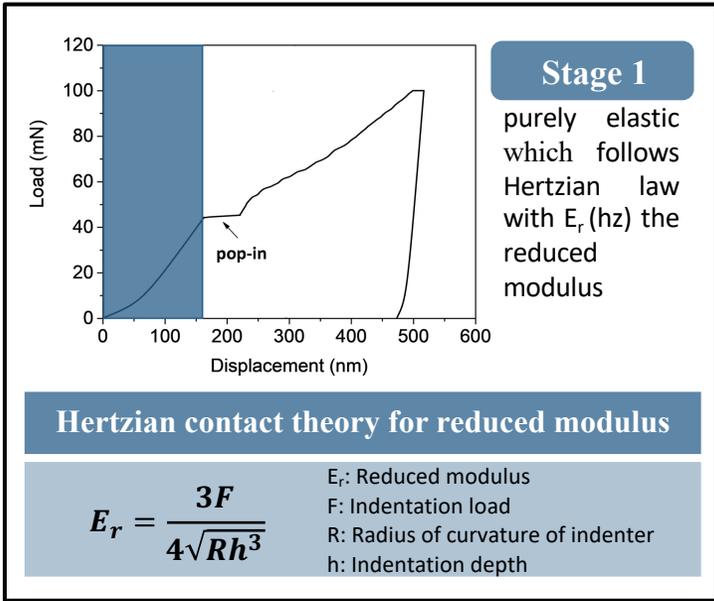
- Solution: 0.1 M NaOH
- Current density: -10 mA/cm<sup>2</sup>
- Duration: 72 hours
- Temperature: 25 °C

### Hydrogen charging ≈ 7 wppm

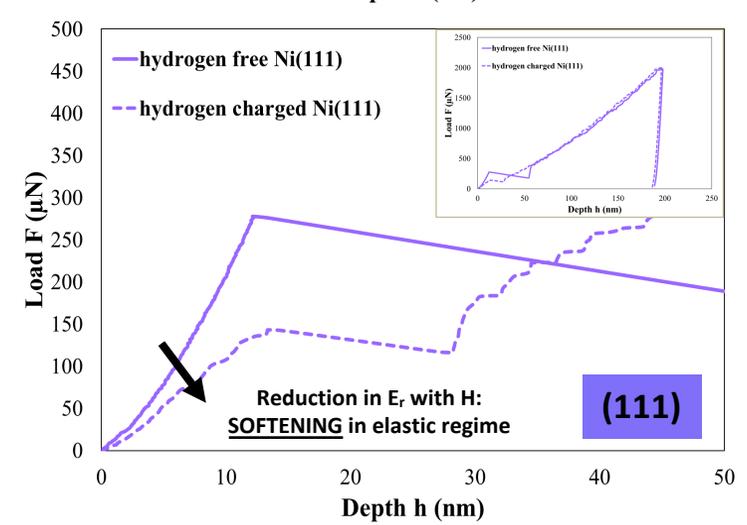
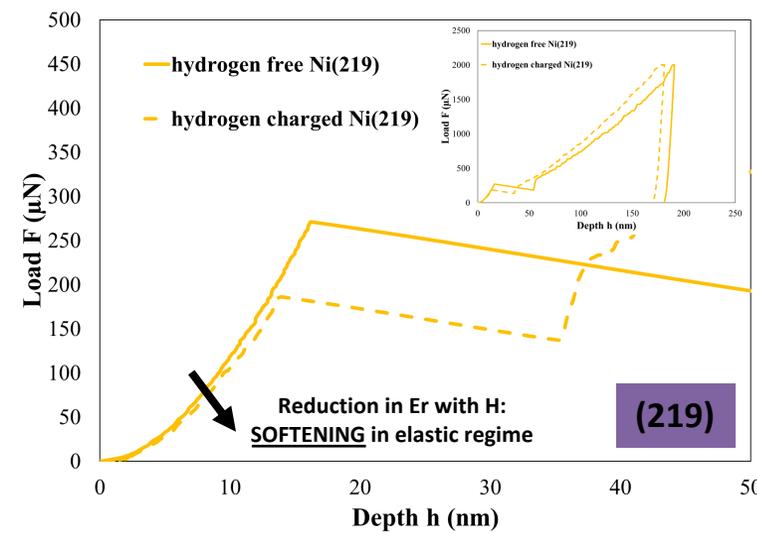
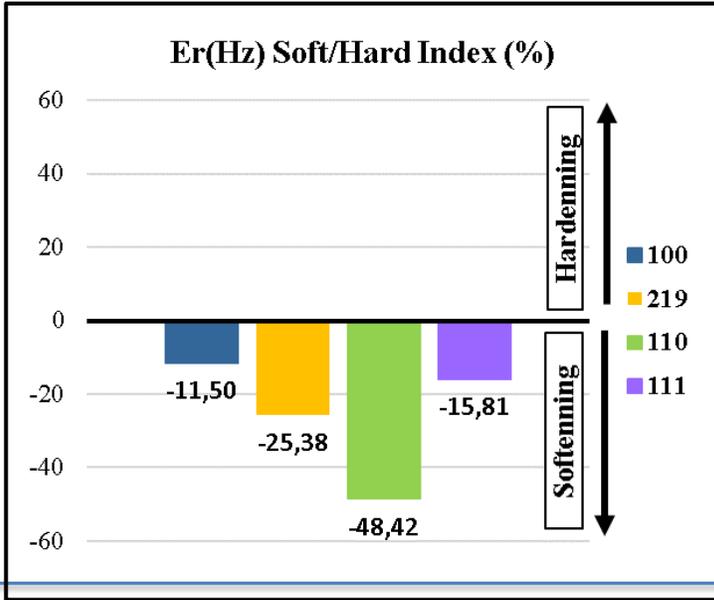
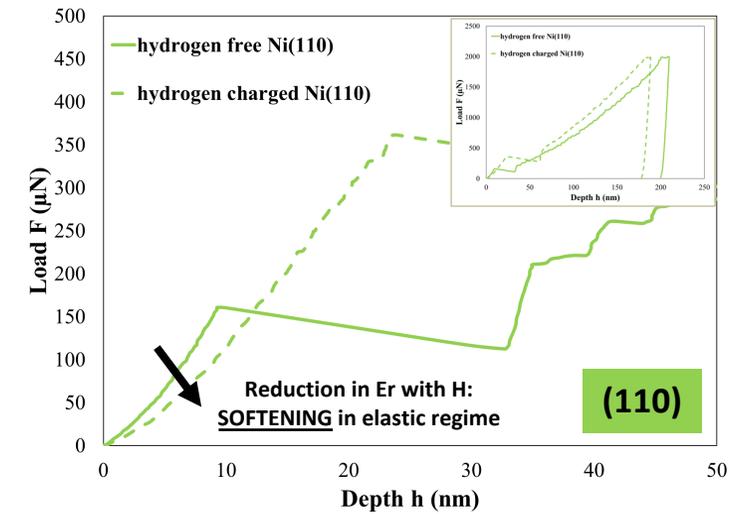
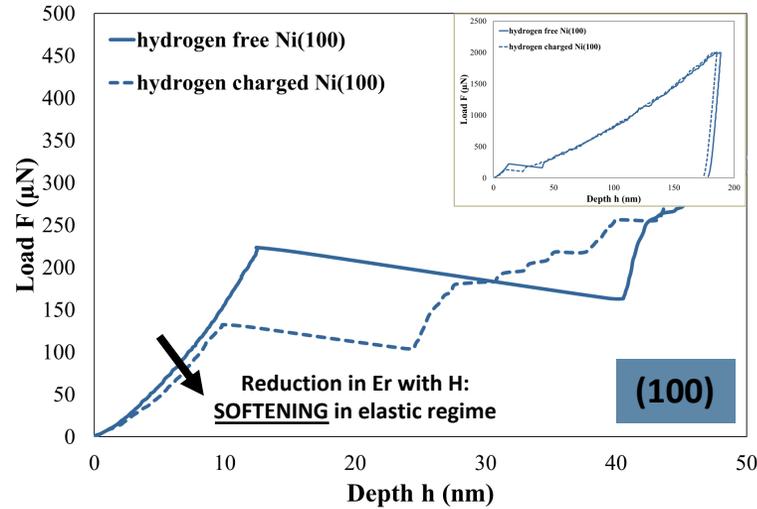
### Nanoindentation

- Micro and NI 50µN to 30N
- Berkovich indenter (R=360nm)
- Load: 2mN
- 25 indentations (5x5 matrix) per condition



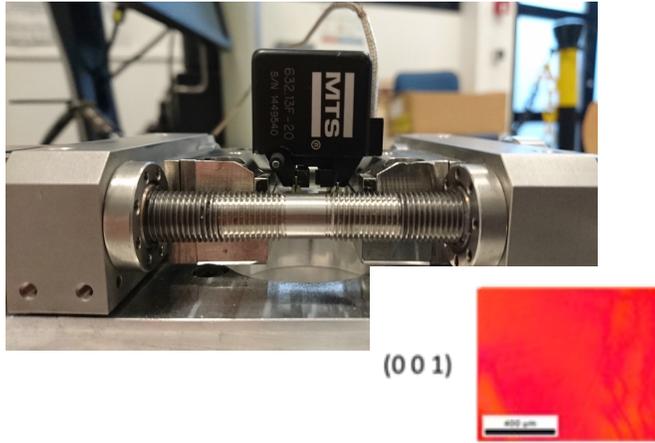


### Ex situ nanoindentation Load-indentation depth curves



H decreases reduced modulus → Softening in all orientations

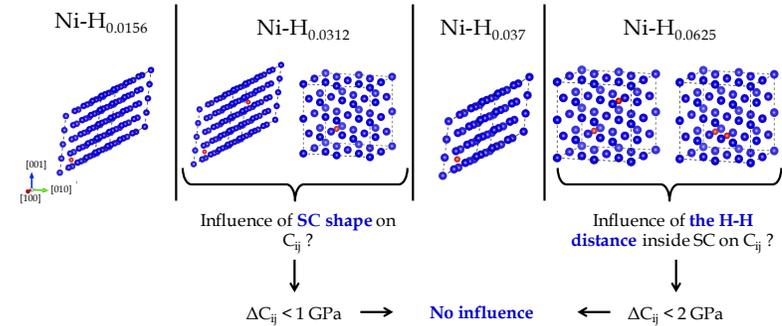
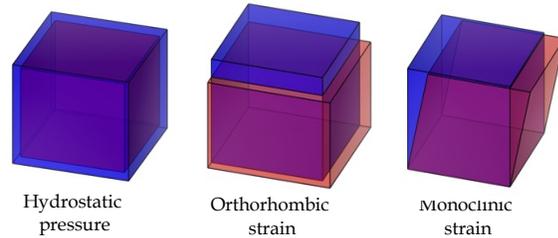
## Tensile tests on Ni (100)



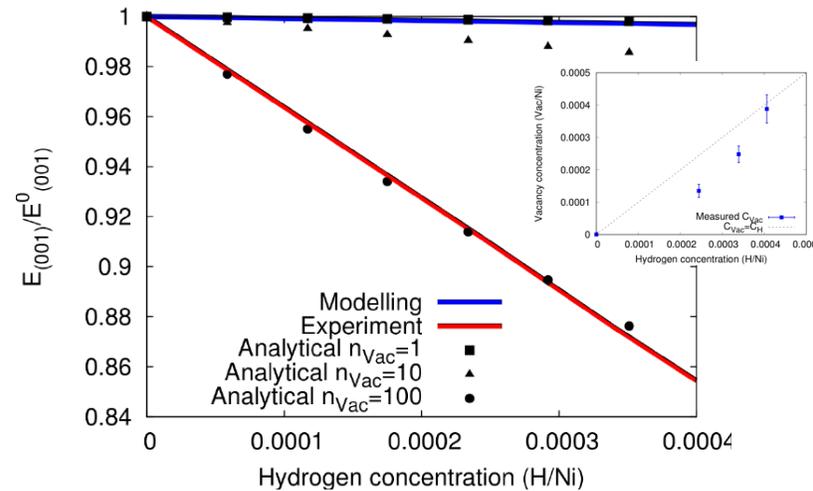
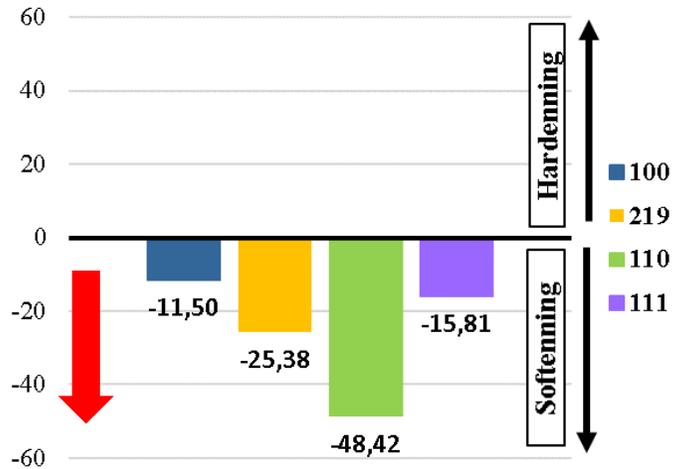
## Softening → Hydrogen decreases elastic modulus?

### Elastic constants of nickel and Ni-H<sub>x</sub> alloys from *ab initio* calculations at finite temperature

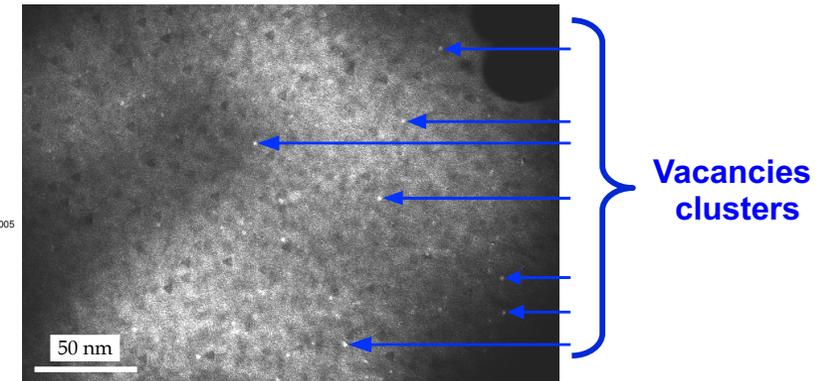
- DFT implemented in the PWSCF code of Quantum Espresso
- Pseudopotentials PAW for Ni and H + PBE-GGA
- Ecutoff = 816 eV (60 Ry)
- Irreducible Brillouin zone sampled on 16×16×16 Monkhorst and Pack grid ( $\Delta E < 10^{-3}$  eV with 20×20×20 grid)
- Self-consistent cycle  $\Delta E < 10^{-8}$  eV



### Er(Hz) Soft/Hard Index (%)

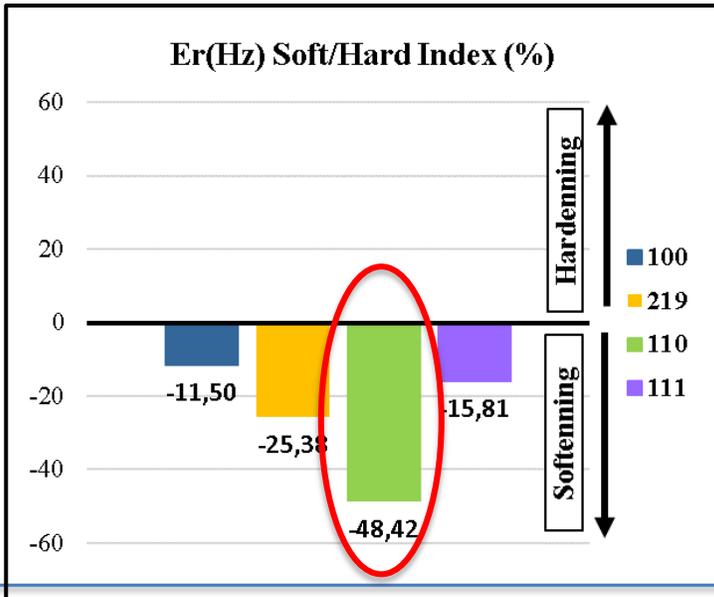
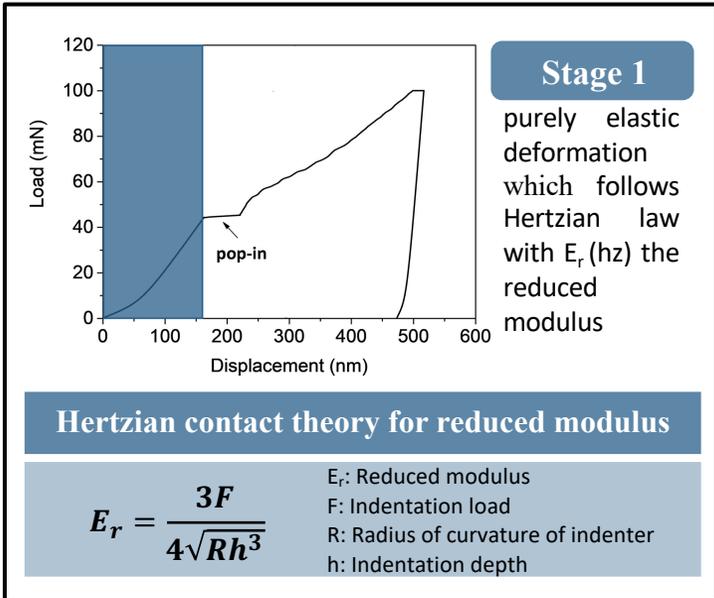


### Ni-H<sub>x</sub> (single crystal)



Hachet et al. Acta Mater. 2018

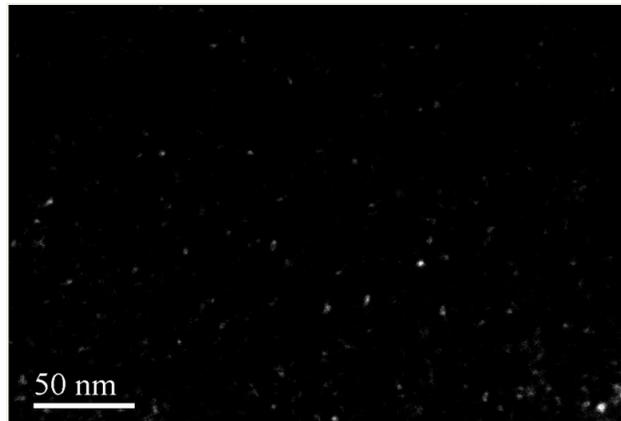
Consequence of vacancies clusters formation!



## TEM Analysis\*

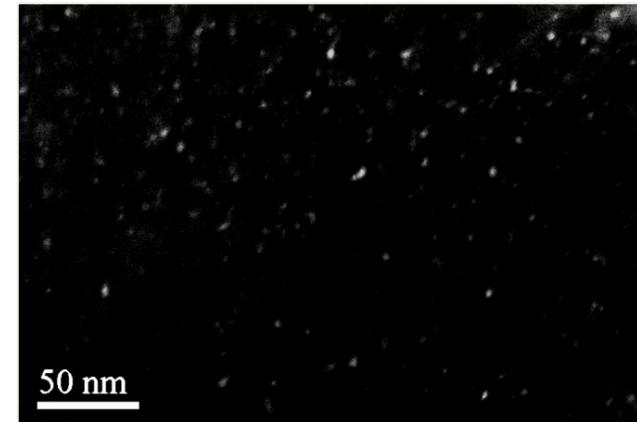
\*Near the surface

Vacancy clusters  
(100) Orientation \_ with H



$$V_{\text{cluster}}/\text{Ni} = 2.45 \cdot 10^{-5}$$

Vacancy clusters  
(110) Orientation \_ with H

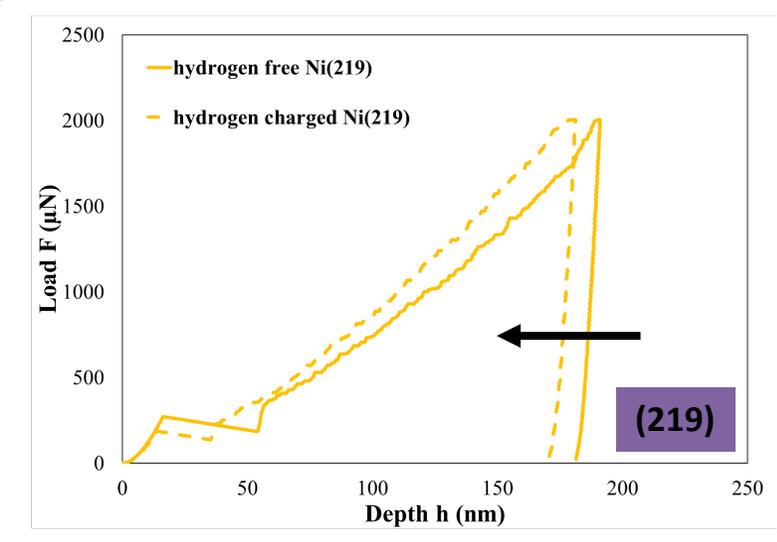
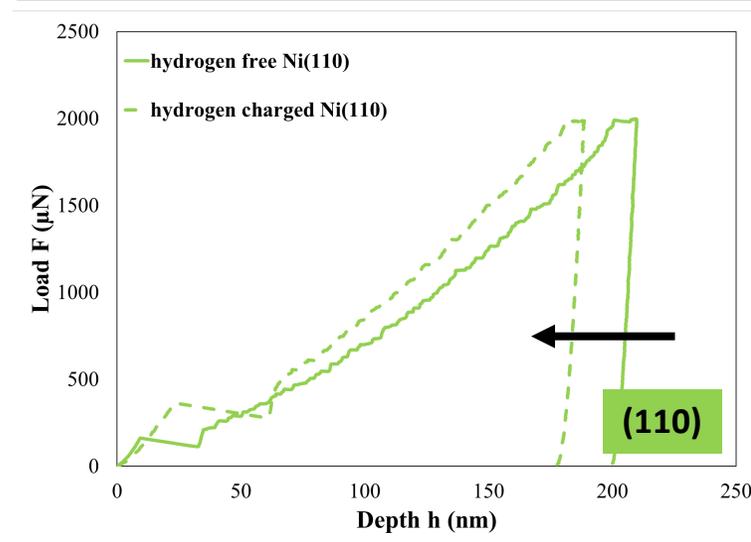
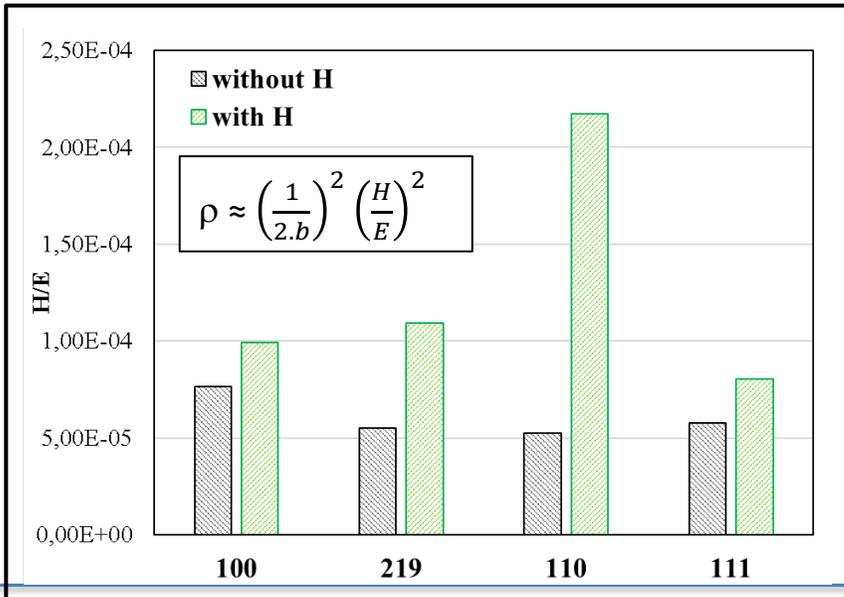
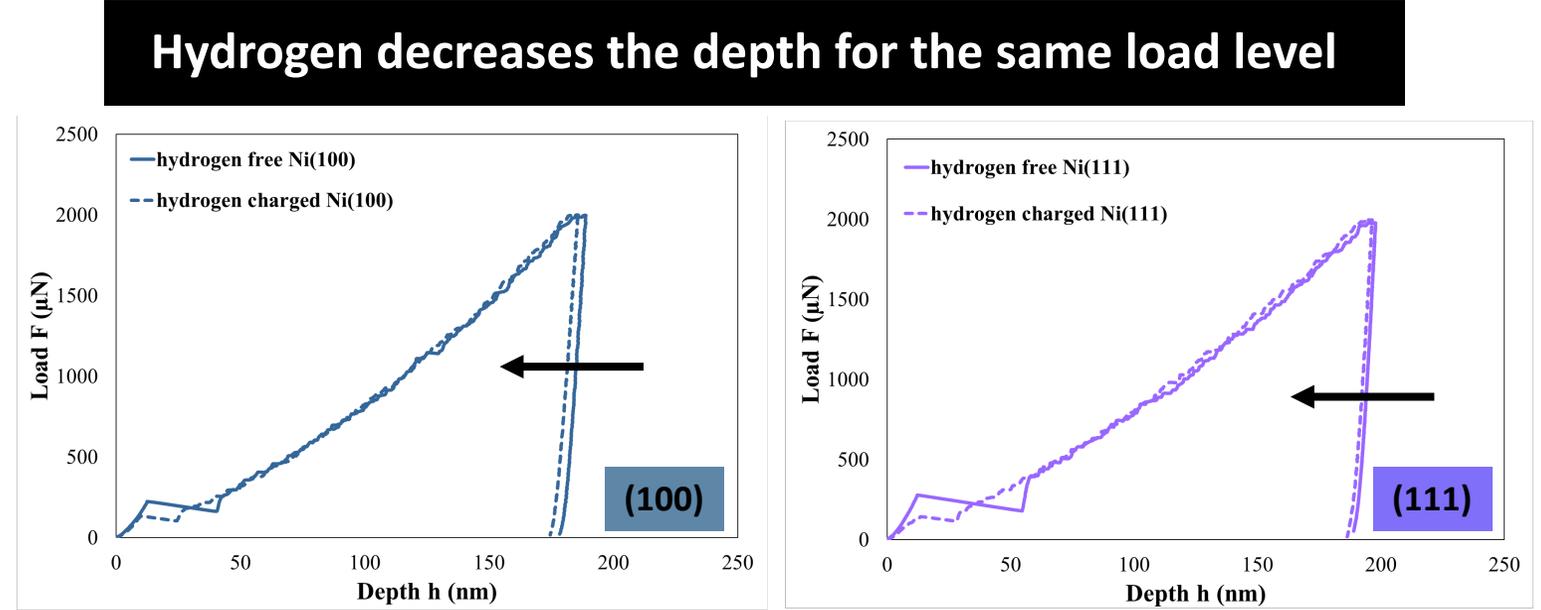
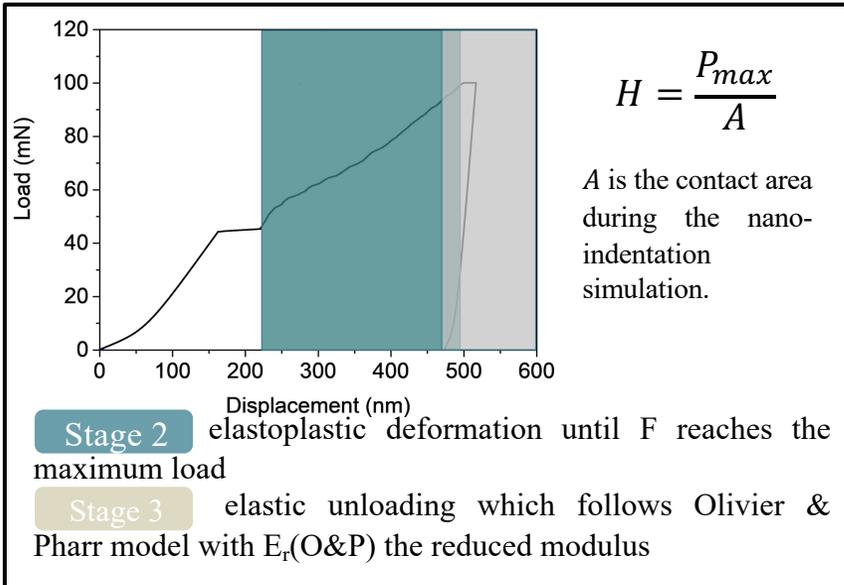


$$V_{\text{cluster}}/\text{Ni} = 4.30 \cdot 10^{-5}$$

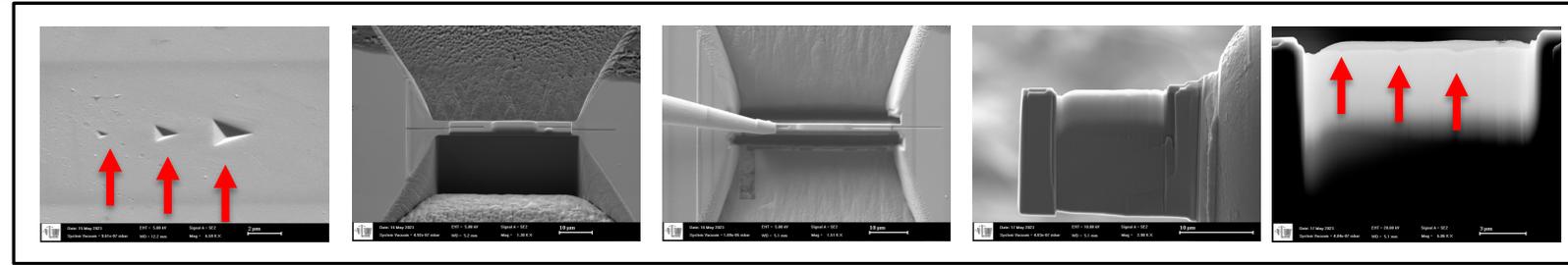
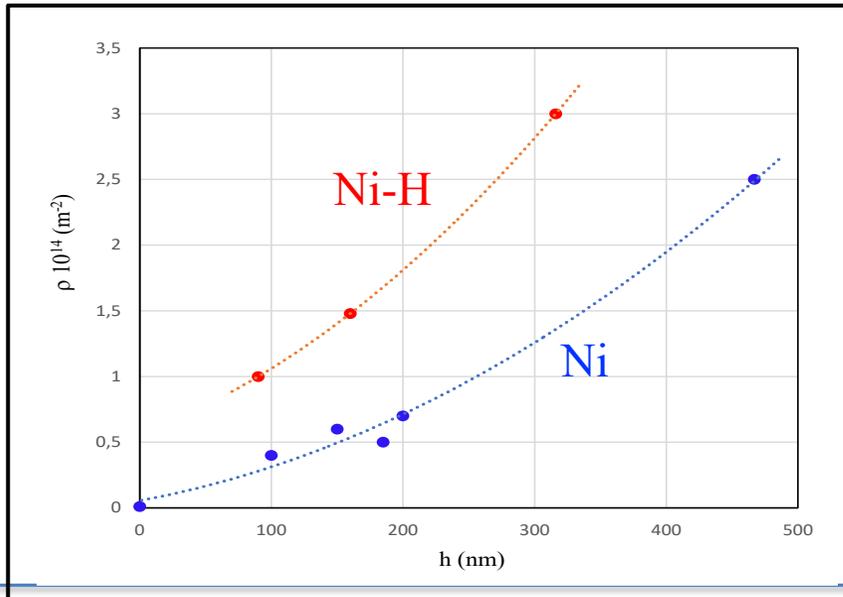
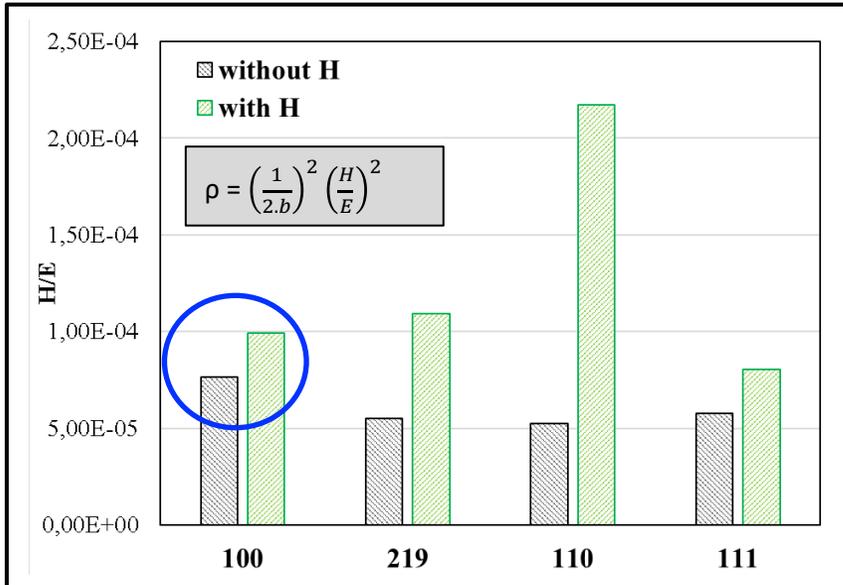
(110) orientation presents a higher vacancy concentration



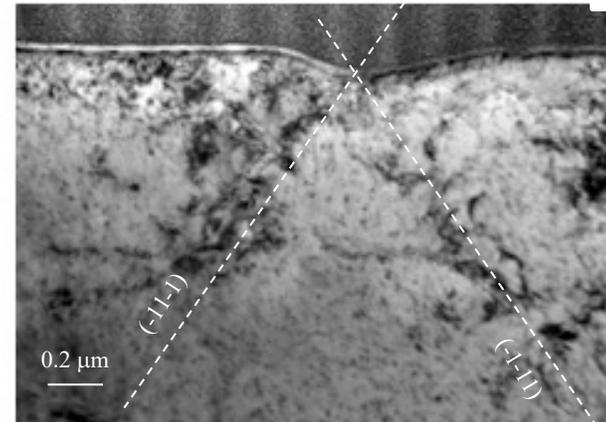
$E_r$  (110) reduction is more pronounced than the other orientations



→ H promotes dislocations multiplication?

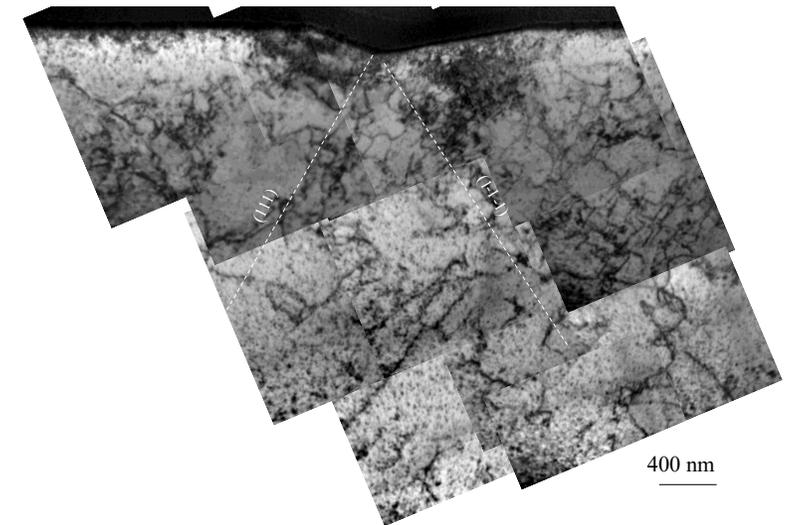


**(100)** Dislocations patterns around the indentation region of (001) Nickel single crystal



Depth equal to 185 nm (2 mN). Diffraction conditions  $g = (200)$  and  $\theta = 7^\circ$ . Tip radius 360 nm.

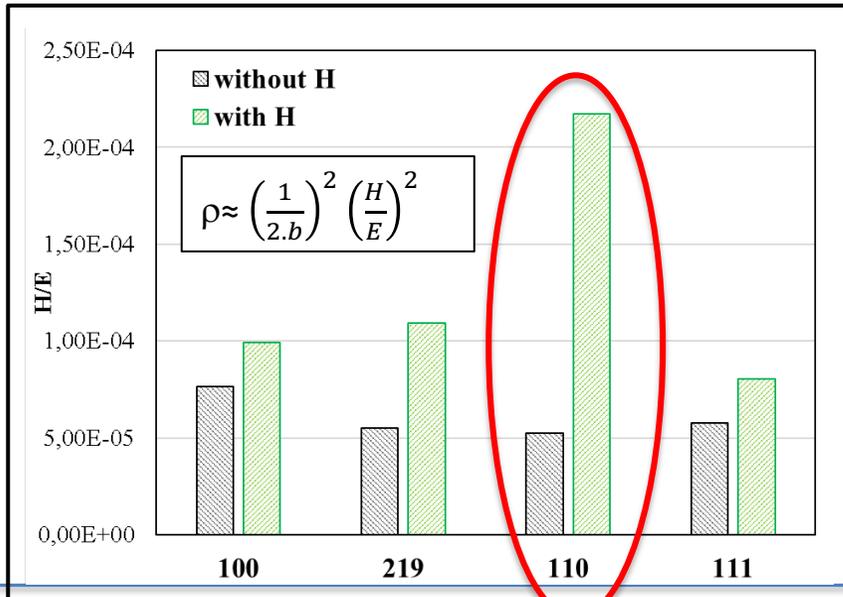
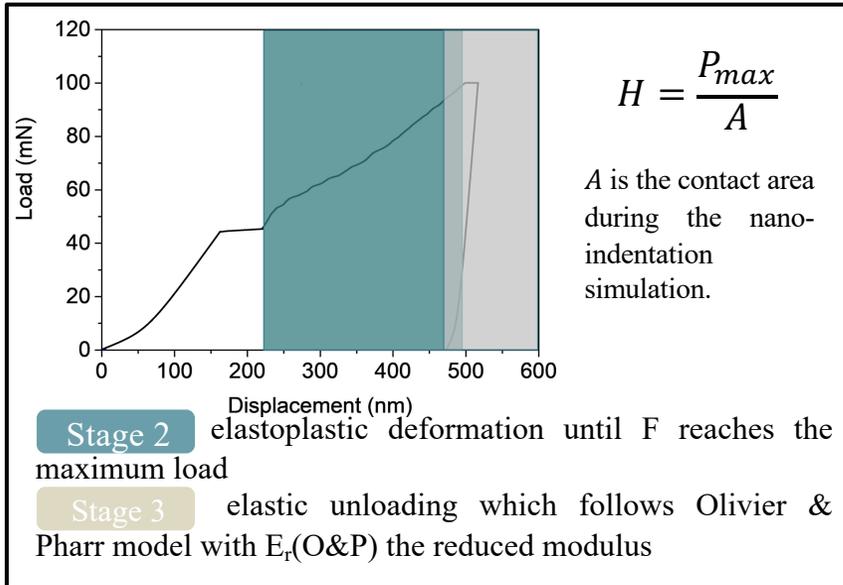
**Ni** →  $\rho = 5 \cdot 10^{13} \text{ m}^{-2}$



Depth equal to 160 nm (2 mN). Diffraction conditions  $g = (-11-1)$  and  $\theta = 20^\circ$ . Tip radius 180 nm.

**Ni-H** →  $\rho = 1.48 \cdot 10^{14} \text{ m}^{-2}$

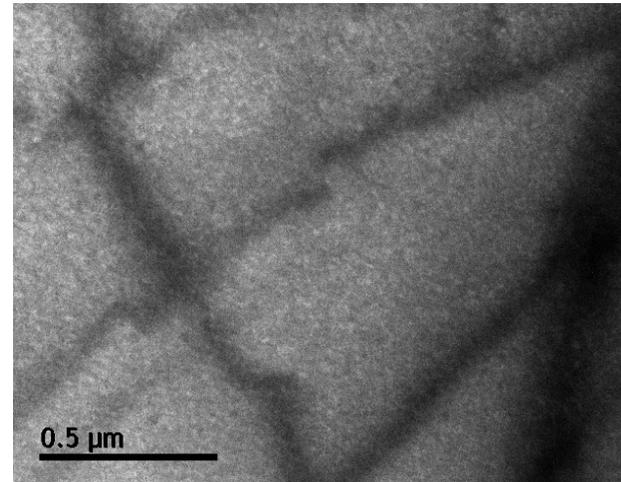
**→ H promotes dislocations multiplication**



### TEM Analysis

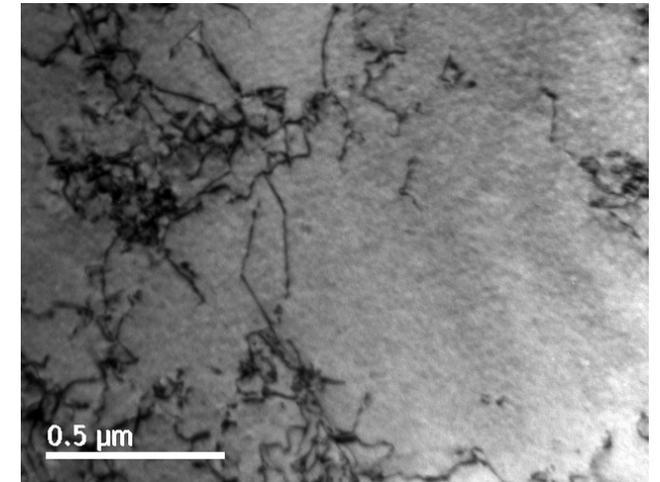
#### Hydrogen effect (near surface)

Dislocations near surface (100) Orientation \_ with H



Ni(100)-H →  $\rho = 0.59 \cdot 10^{14} \text{ m}^{-2}$

Dislocations near surface (110) Orientation \_ with H

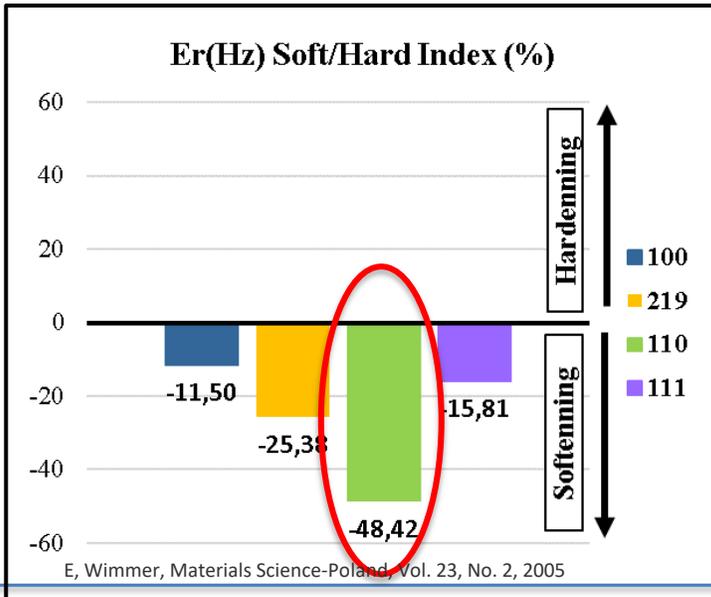
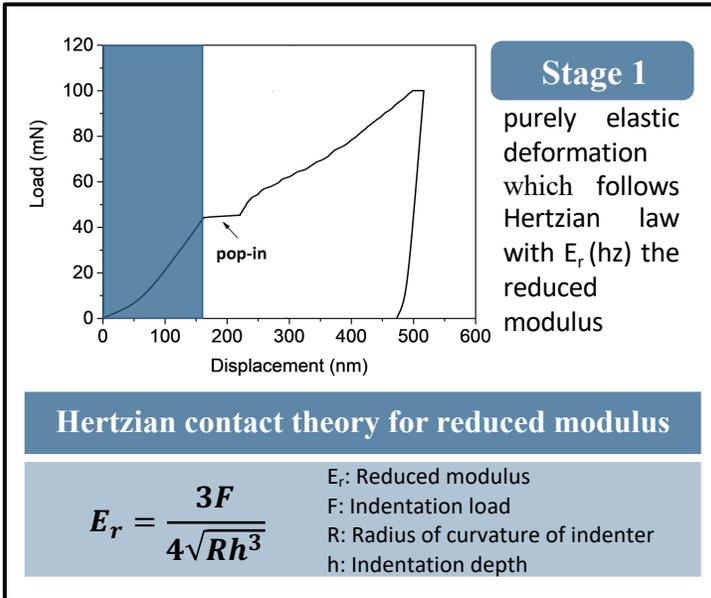


Ni(110)-H →  $\rho = 1.84 \cdot 10^{14} \text{ m}^{-2}$

(110) orientation presents a higher dislocation density in presence of H



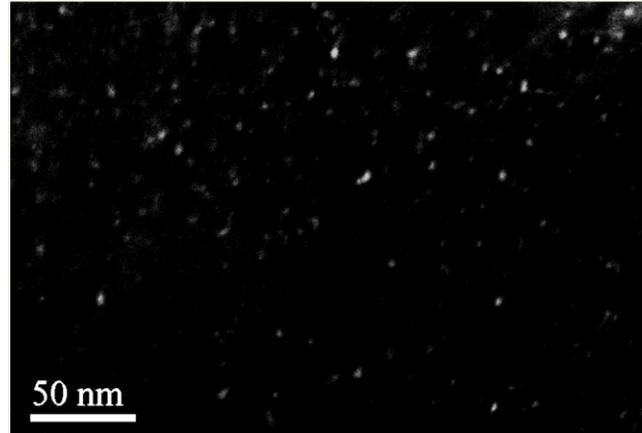
H/E (110) is more pronounced than the other orientations



## TEM Analysis\*

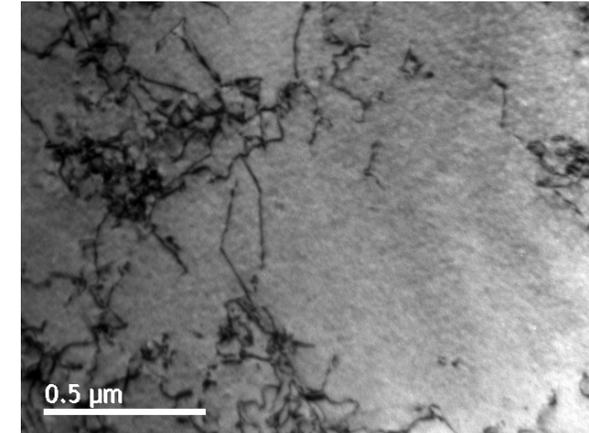
\*Near the surface

**Vacancy clusters  
(110) Orientation \_ with H**



$$V_{\text{cluster}}/\text{Ni} = 4.30 \cdot 10^{-5}$$

**Dislocations near surface  
(110) Orientation \_ with H**

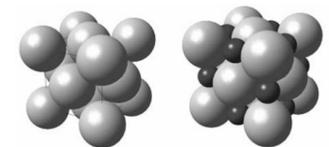


$$\rho = 1.84 \cdot 10^{14} \text{ m}^{-2}$$

**Nickel hydride  
impact on the elastic modulus**

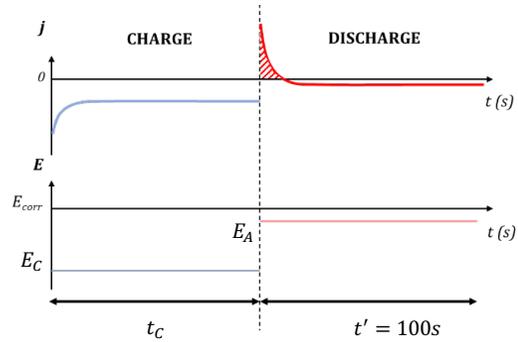
Parameter	Ni	Ni-Hydride
Lattice parameter (Å)	3.50	3.72
Young's modulus (GPa)	254	116

Ratio of -54%



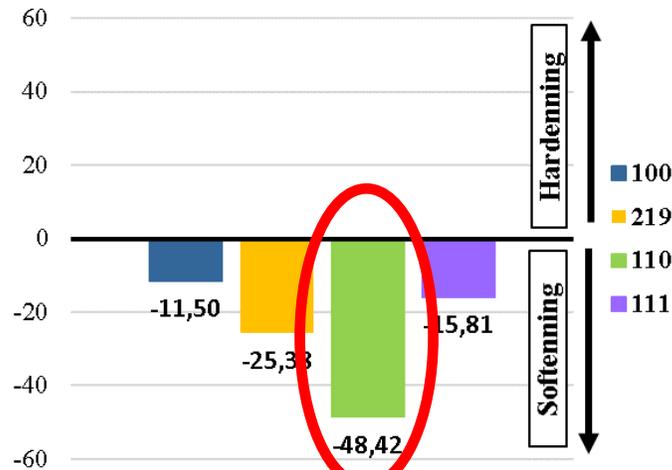
# Anisotropic behavior?

## Pulse electrochemistry



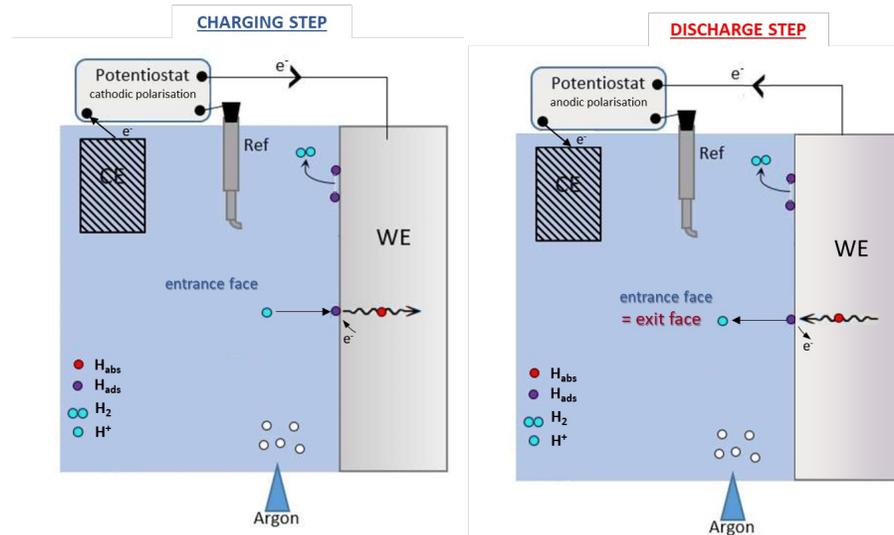
- Cathodic potential imposed  $E_c = -350 \text{ mV/SHE}$
- H-coverage:  $\theta = 25 \%$
- Charging time  $t_c$ :  $2 \text{ s} \leq t_c \leq 600 \text{ s}$

## Er(Hz) Soft/Hard Index (%)



## Anisotropic effect of Hydrogen → Diffusion?

### Procedure



Illustrations adapted from M. Duportal PhD Thesis 2020

**Experimental setup:**  $\text{H}_2\text{SO}_4$  1M at  $18^\circ\text{C}$  (291 K) / Ar deaeration / Pt Counter Electrode / ESS Reference Electrode

C. Traisnel, PhD (2018-2022)

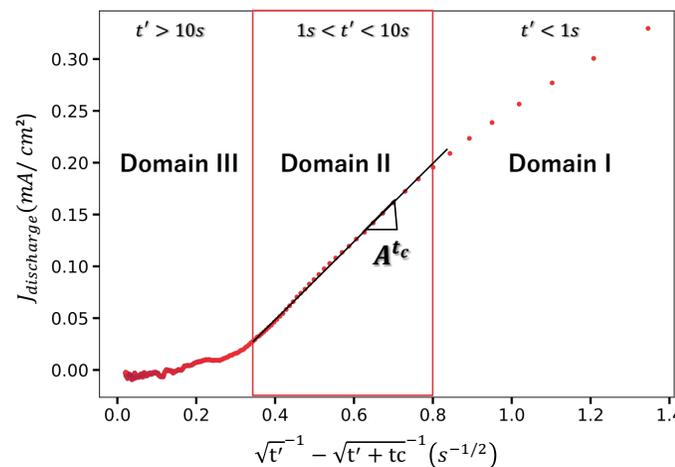
## Fick laws solution under diffusion control (discharge)<sup>1</sup>:

without trapping

$$j_{\text{Discharge}} = A^{t_c} \left( \frac{1}{\sqrt{t'}} - \frac{1}{\sqrt{t' + t_c}} \right) \text{ with } A^{t_c} = F C_S \sqrt{\frac{D_{app}^{t_c}}{\pi}}$$

$$\bar{x} = \sqrt{2D_{app}^{bulk} t_c}$$

→  $D_{app}^{t_c}$ ?  $\bar{x}$ ?



<sup>1</sup> B.G. Pound et al., 1987.

# Anisotropic behavior?

$D_{app}^{bulk}\{hkl\}$  from J.Li PhD Thesis, 2018

{100} →  $6 \times 10^{-14} \text{ m}^2/\text{s}$

{110} →  $11 \times 10^{-14} \text{ m}^2/\text{s}$

{111} →  $16 \times 10^{-14} \text{ m}^2/\text{s}$

Local apparent diffusion coefficient estimation:

$$D_{app}^{tc} = \left( \frac{\overline{A^{tc}}}{A^{bulk}} \right)^2 D_{app}^{bulk}$$

$A^{bulk} = A^{60-600s}$

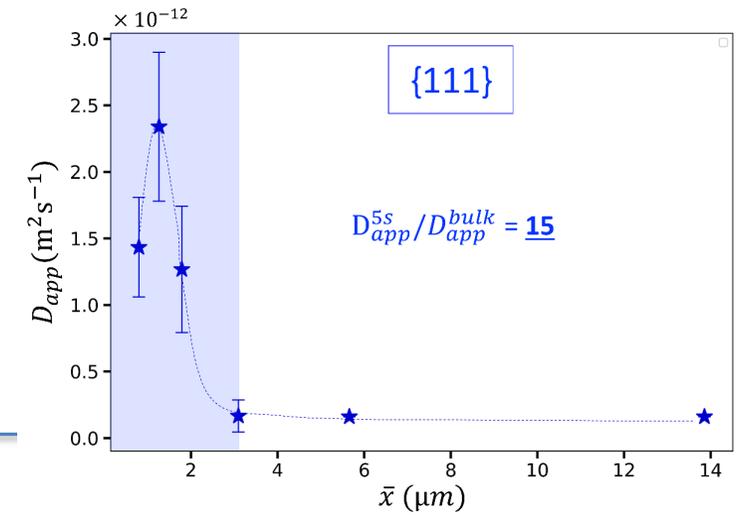
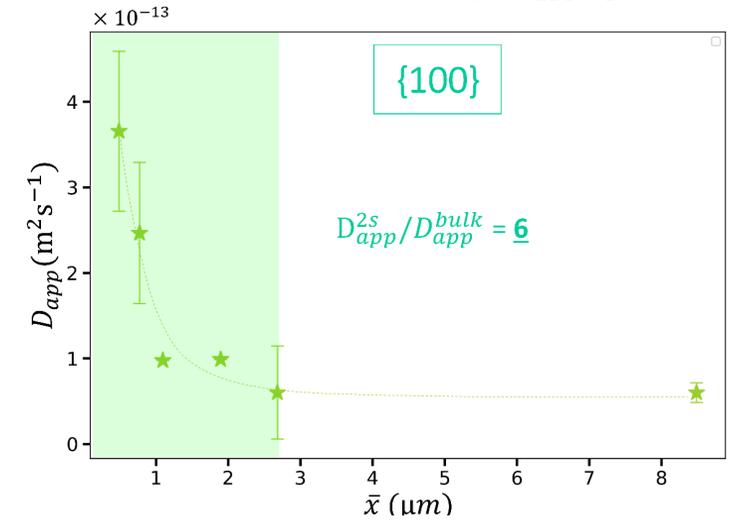
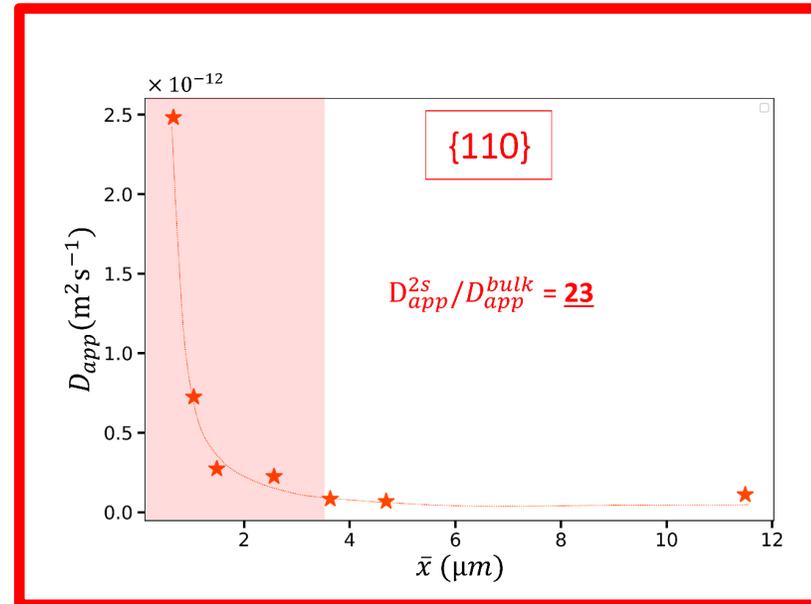
## Anisotropic effect of Hydrogen → Diffusion?

$$j_{Discharge} = A^{tc} \left( \frac{1}{\sqrt{t'}} - \frac{1}{\sqrt{t' + t_c}} \right) \quad \text{with} \quad A^{tc} = F c_s \sqrt{\frac{D_{app}^{tc}}{\pi}}$$

Mean depth investigated:

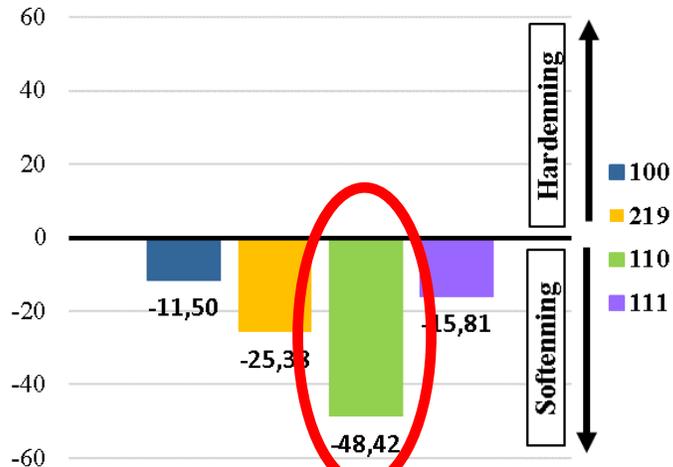
$$\bar{x} = \sqrt{2D_{app}^{bulk} t_c}$$

Hypothesis: H coverage similar ↔  $c_s$  constant



C. Traisnel, PhD (2018-2022)

Er(Hz) Soft/Hard Index (%)

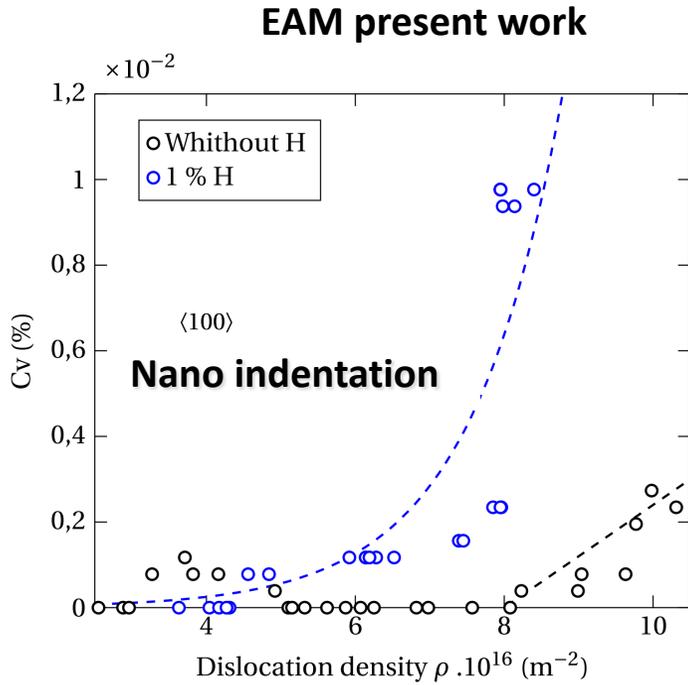
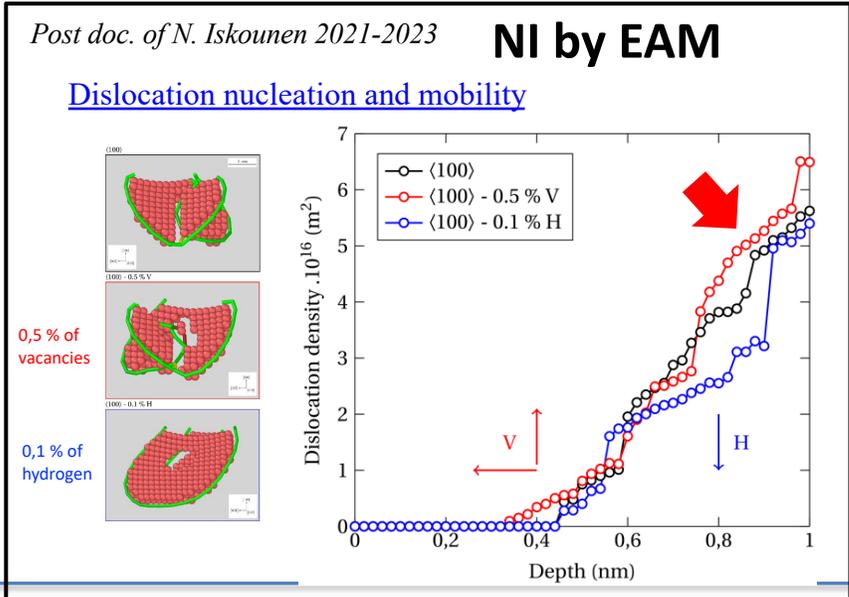
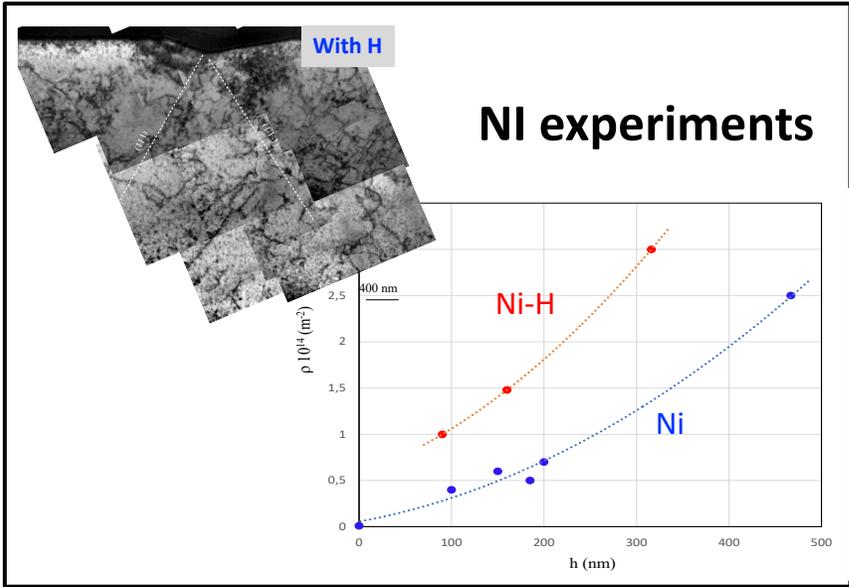


<sup>1</sup> B.G. Pound et al., 1987.

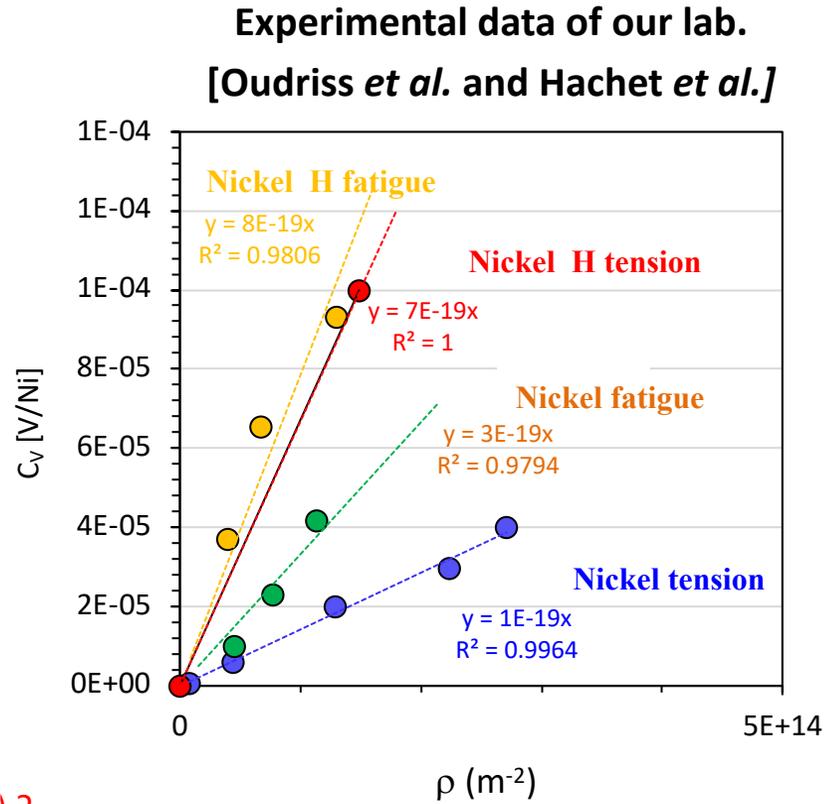
## Correlation between dislocations and vacancies?

### Hydrogen enhanced strain-induced vacancy

(100)



Testing type effect (homogenous vs gradient) ?



*In progress ...*

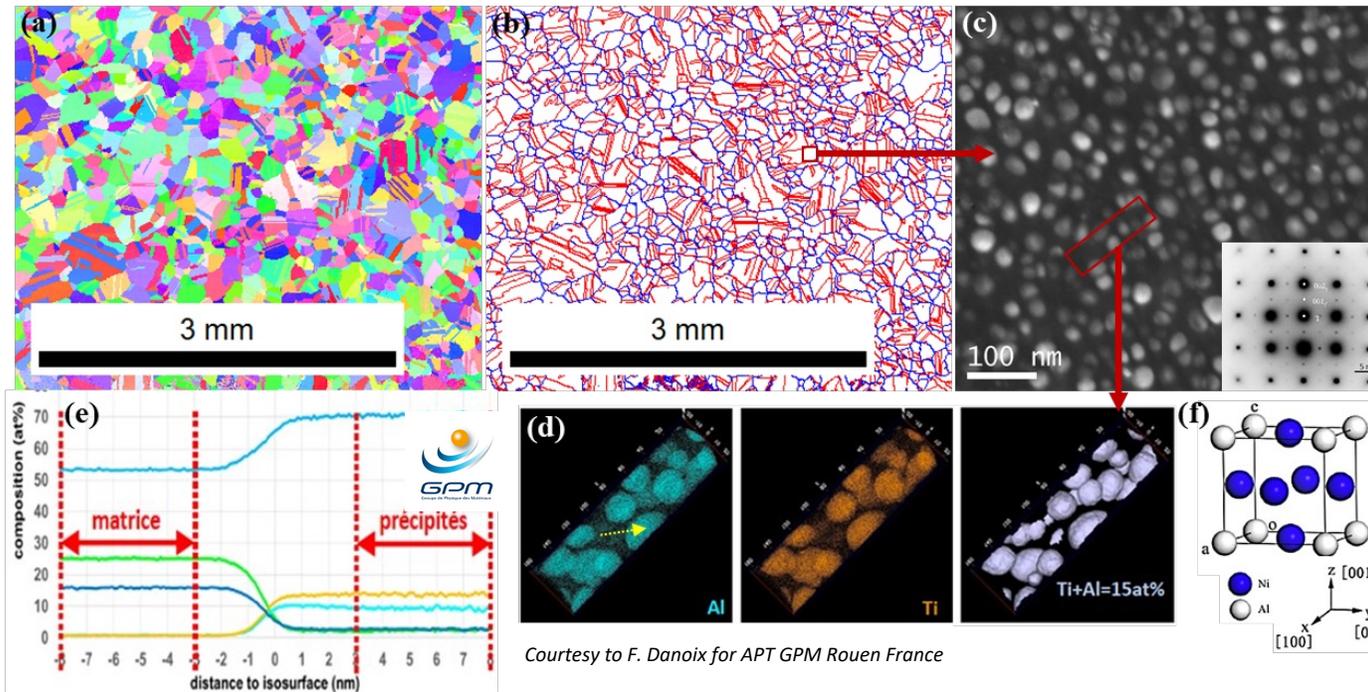
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## *Hydrogen vs. Precipitates*

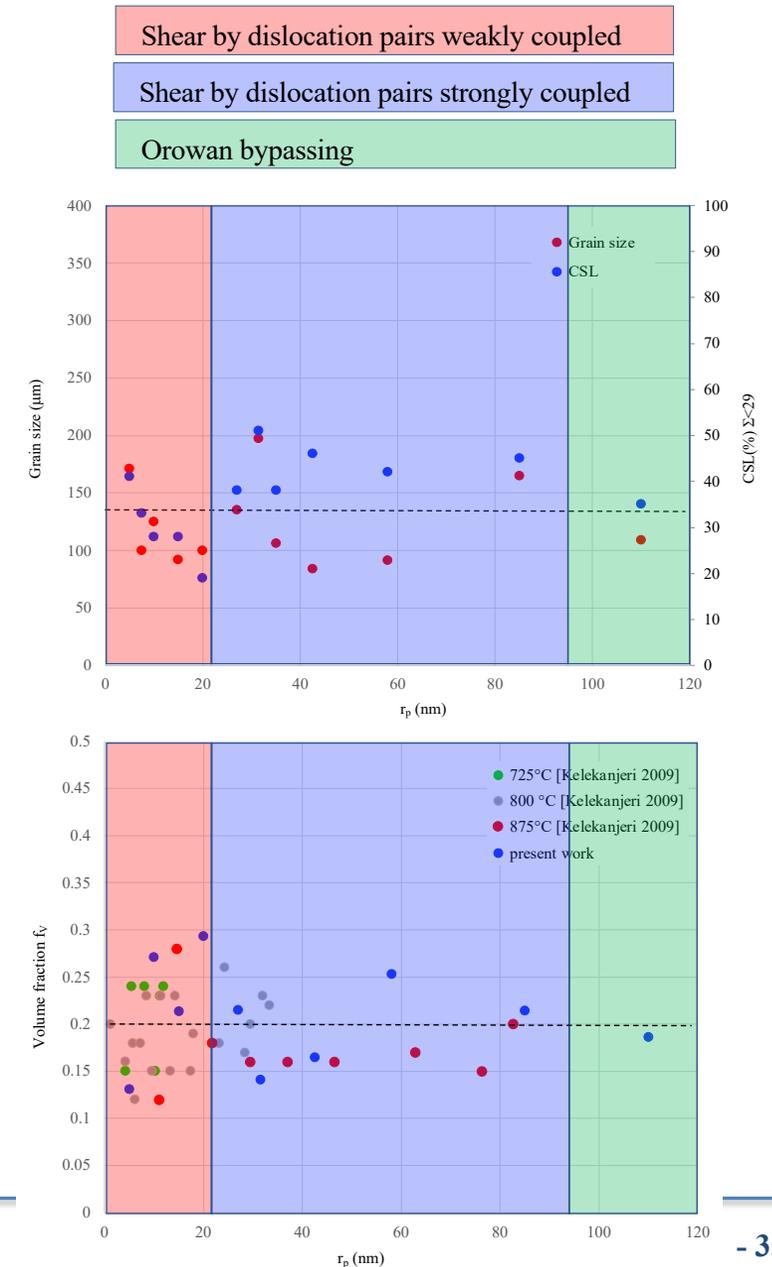
12 Waspaloy –  $\gamma'$  Ni<sub>3</sub>(Al, Ti) : different ageing treatments several precipitates sizes (radius: 5 to 110 nm), same volume fraction of precipitate (20%), same grains size (140  $\mu$ m) and CSL fraction (37%).

Ni	Al	Ti	Co	Cr	Mo	Fe	Zr	C	Mn	Cu	Si	P	S	B
58.1	1.35	3.13	14	19.05	4.13	0.08	0.075	0.033	0.02	<0.01	<0.02	0.003	0.002	52 *

**Solution heat treatment** in an air muffle furnace at 1080 °C for 4 hours, followed by oil quenching. Subsequent **aging treatment** in a tubular furnace filled with argon at different temperatures and durations



Multi-scale microstructural representation of W4: (b) EBSD-IPF; (b) TEM dark field image  $\gamma'$ -precipitates and diffraction pattern in inset; (c,e) APT-chemical composition analysis of  $\gamma'$  precipitates; (d) schematic representation of  $\gamma'$ -precipitate crystal; (f) size distribution of  $\gamma'$ -precipitates.

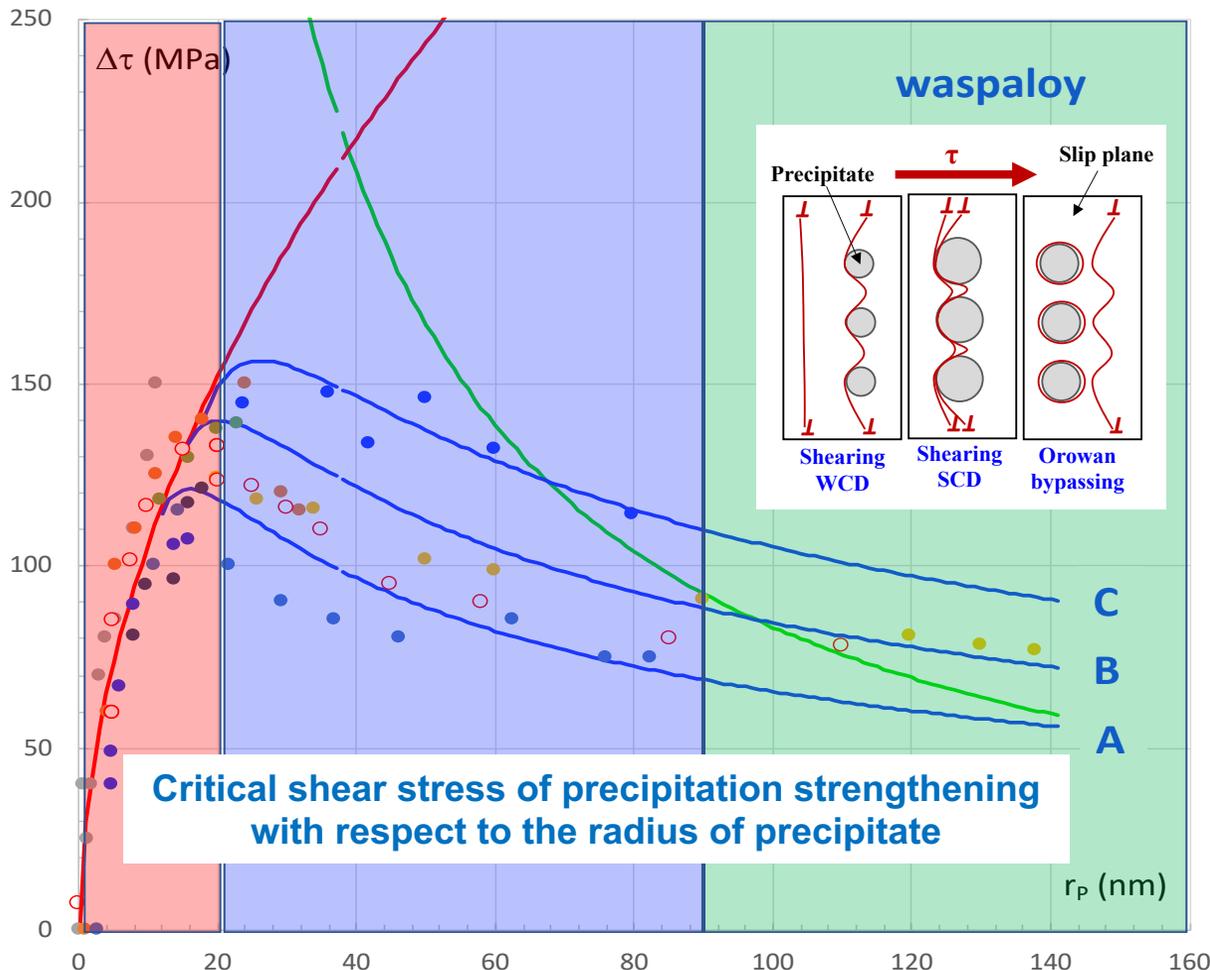


### Critical shear stress of precipitation strengthening

Based on Vickers microhardness  $H_v$ , yield stress  $\sigma_0 = 3 \cdot H_v$ ,

Critical shear stress  $\tau_0 = \sigma_0 / M$  ( $M = 3.03$ ) and Contribution of precipitate,

$\Delta\tau = \tau_0 - \tau_{0(TTA)}$  ( $\tau_{0(TTA)}$  without precipitate)



$\mu$ (GPa)	$b$ (nm)	$f_V$ (%)	$\gamma_{APB}$ (mJ/m <sup>2</sup> ) R1	$\gamma_{APB}$ (mJ/m <sup>2</sup> ) R2	$w$
81	0.254	20	130	115	1.4

### Domain-1 with $r_p < 20$ nm

Weekly-coupled shearing (WCD)

$$\Delta\tau_{wpc} = \frac{\gamma_{APB} \sqrt{f_V}}{2b} \left( \left[ \frac{6\gamma_{APB}}{\pi T} \right]^{1/2} \sqrt{r} - \sqrt{f_V} \right)$$

### Domain-2 with $20 \text{ nm} < r_p < 90 \text{ nm}$

Strongly-coupled shearing (SCD)

$$\Delta\tau_{spc} = \sqrt{\frac{3f_V}{2}} \left[ \frac{\mu b}{r} \right] \frac{w}{\pi^{3/2}} \left( \left[ \frac{\pi \gamma_{APB}}{w T} \right] r - 1 \right)^{1/2}$$

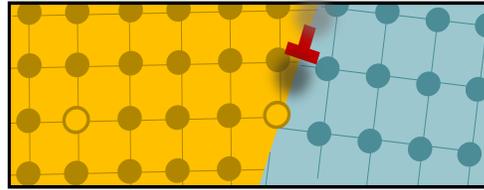
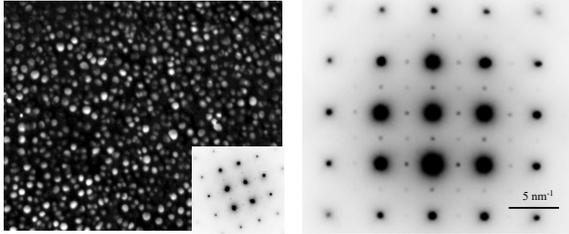
### Domain-3 with $r_p > 90$ nm

Orowan bypassing by looping

$$\Delta\tau_{orowan} = \sqrt{f_V} \left[ \frac{\mu b}{2r} \right] \left( \sqrt{\frac{2\pi}{3}} - 2\sqrt{f_V} \right)$$

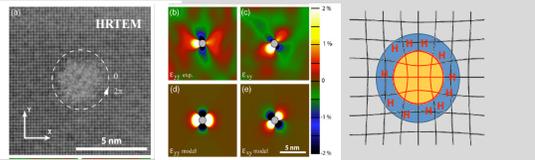
⇒ hydrogen impact on the three processes ?

Waspaloy



Waspaloy –  $\gamma'$  Ni<sub>3</sub>Al (f<sub>v</sub>=25%), Grain size 50  $\mu$ m  
Inconel 718 AM –  $\gamma''$   
Electrochemical charging (NaOH 0.1M, 300 K, 10 mA/cm<sup>2</sup>)

$$\delta = \frac{2(a_{\gamma'} - a_{\gamma})}{(a_{\gamma'} + a_{\gamma})}$$



“Misfit”  $\delta = \frac{b_{pre} - a_{matrix}}{a_{matrix}}$

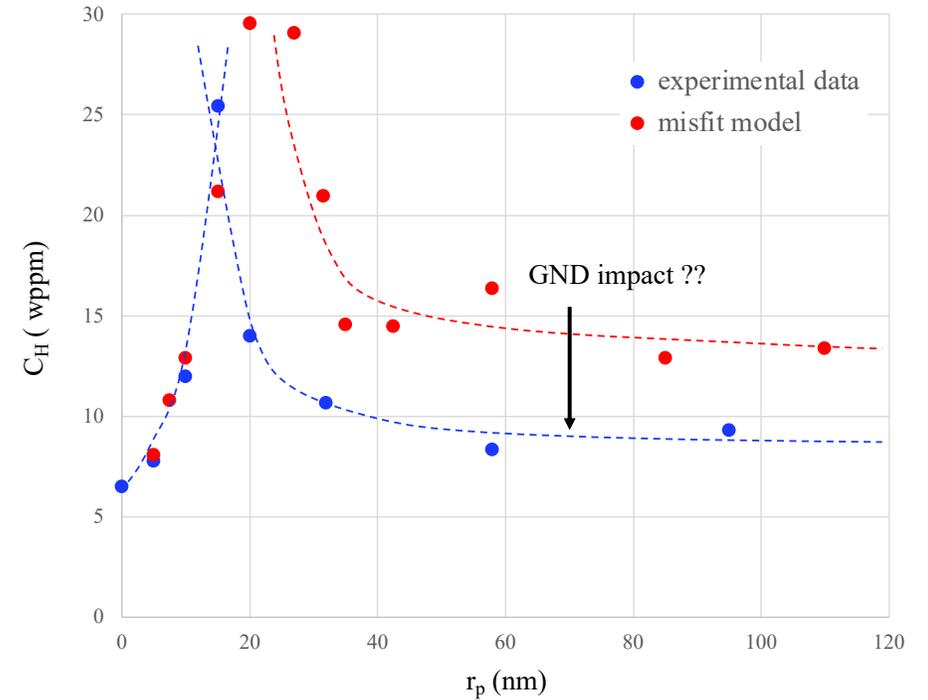
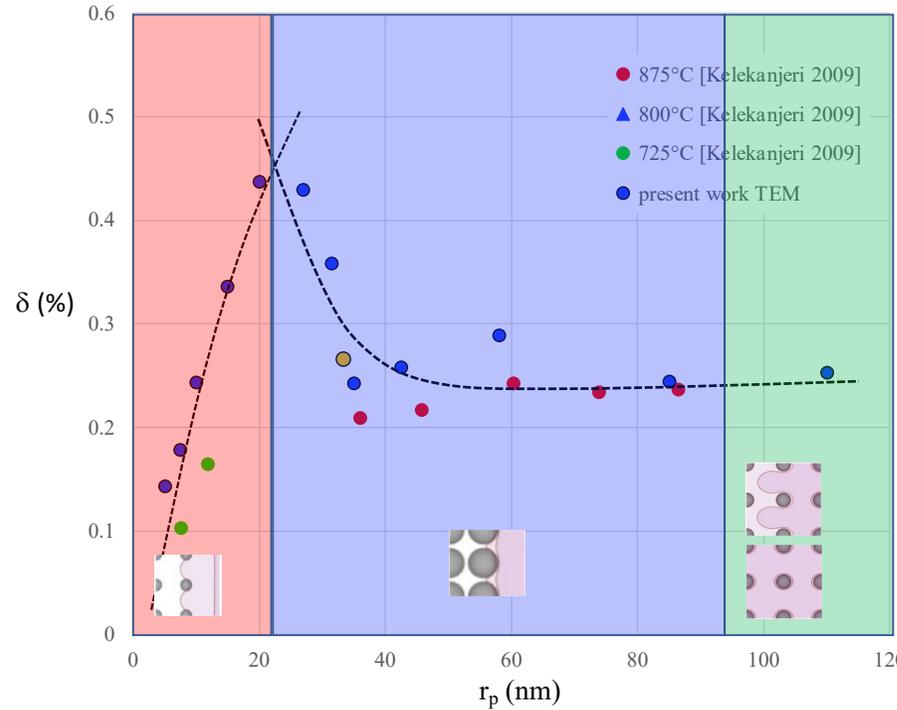
$$\varepsilon_m = \frac{2}{3} \delta \left[ \frac{r_p}{\Delta r} \right]^3 \quad \sigma_m = \left( \frac{E}{1-2\nu} \right) \varepsilon_m$$

$$\frac{s(r)}{s_0} = \exp\left( \frac{\sigma_m V_H}{k_B T} \right)$$

$$\frac{C_{Tr}}{C_L} = f_p \cdot \frac{\Delta V}{V_p} \cdot \frac{1}{\Delta r} \int_{r_0}^{r_0+\Delta r} \frac{s(r)}{s_0} dr$$

« Macroscopic » solubility      « Microscopic » solubility

r<sub>p</sub> precipitate radius, Δr crite radius



- ✓ Excess of hydrogen solubility due to elastic distortions associated with the precipitates (coherent/ semi-coherent) : first regime only !
- ✓ Possible accommodation of strain field by geometrical necessary dislocations (GND)

# Hydrogen – mechanical behaviour

Shear by dislocation pairs weakly coupled :  $r_p < 20$  nm

Shear by dislocation pairs strongly coupled:  $20 \text{ nm} < r_p < 90$  nm

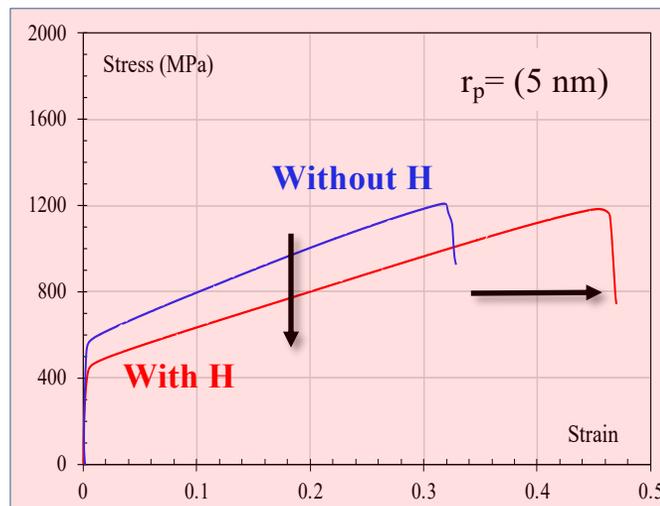
Orowan bypassing :  $r_p > 90$  nm

## Based on Vickers microhardness Hv

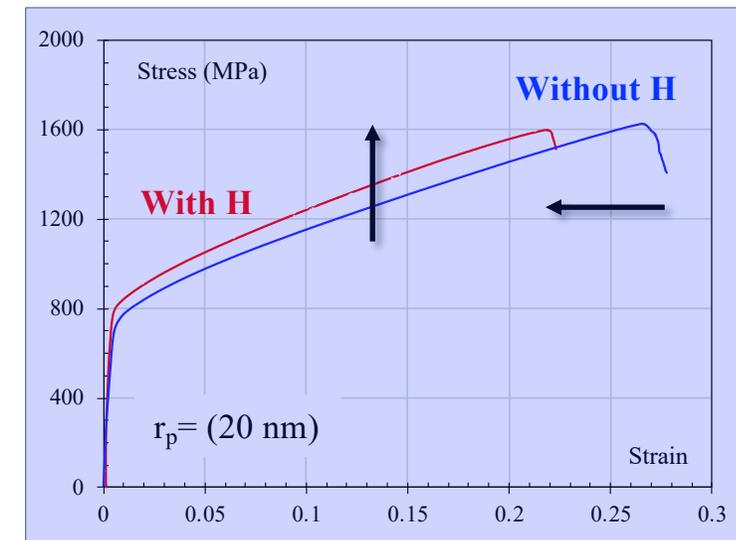
	DOMAIN I	DOMAINE II	DOMAIN III
HV	362	336	318
HV (H)	385	350	336
$\Delta\tau$	105	79	54
$\Delta\tau$ (H)	130	94	80
APB	130	115	
APB (H)	150	130	
$r_p$ (nm)	10	58	110
$r_{ap}$ (nm)			100

APB Anti Phase Boundary

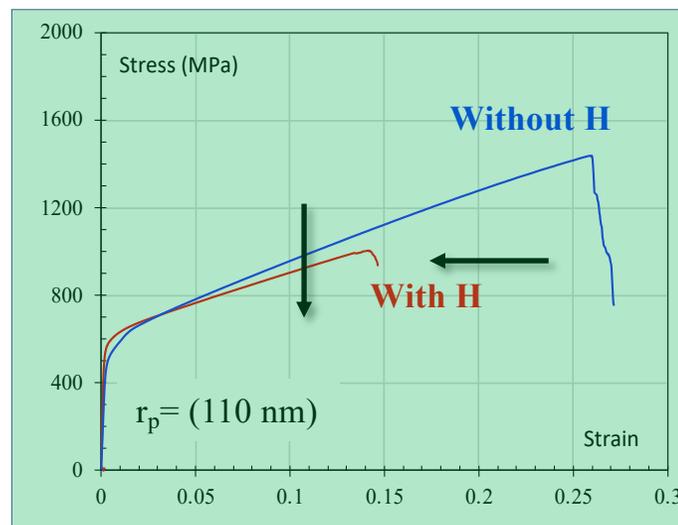
- ✓ Shearing domains: an increase of APB energy
- ✓ Orowan's bypassing domain: a decrease of apparent precipitate size (screening of elastic interactions)



- ✓ Stress softening
- ✓ Increase of ductility



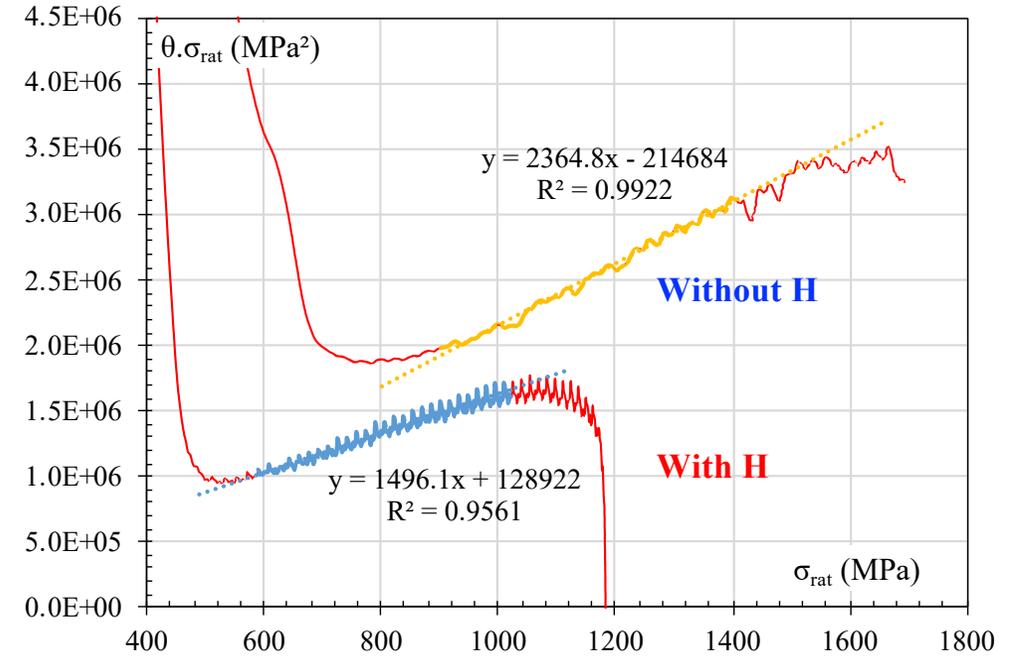
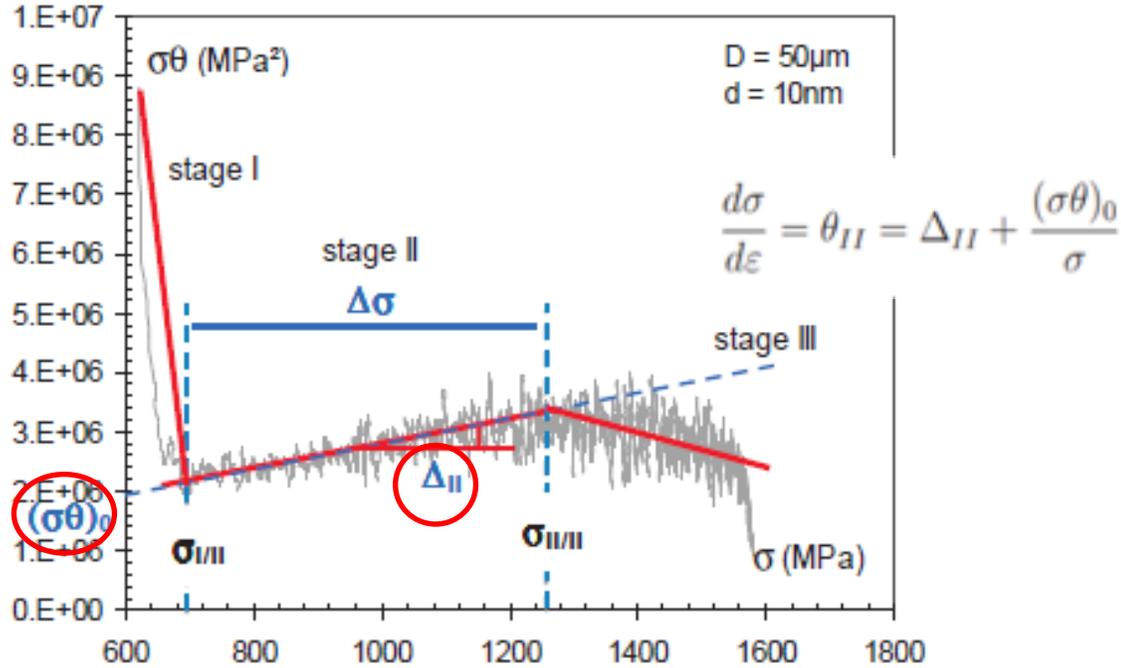
- ✓ Stress hardening
- ✓ lost of ductility



- ✓ Stress softening
- ✓ lost of ductility

## Complexes relations between hardening/softening and ductility

Post-Doc S.P. Murugan (2022-2023)



### Kocks-Mecking model

$$\sigma = \alpha \mu b M \sqrt{\rho}$$

$$\frac{d\rho}{d\varepsilon} = \frac{M\sqrt{\rho}}{\beta b} + \frac{Mk_g}{bd} + \frac{M}{bL} - \frac{2MPy}{b}$$

$$\sigma\theta = \frac{\alpha\mu M^2}{2\beta}\sigma + \frac{\alpha^2\mu^2 M^3 b}{2}\left\{\frac{k_g}{d} + \frac{1}{L}\right\} - \alpha^2\mu^2 b M^3 Py$$

$$\frac{d\sigma}{d\varepsilon} = \theta_{II} = \Delta_{II} + \frac{(\sigma\theta)_0}{\sigma}$$

$$\Delta_{II} = \frac{\alpha\mu M^2}{2\beta}$$

$$(\sigma\theta)_0 = \frac{\alpha^2\mu^2 M^3 b}{2}\left\{\frac{k_g}{d} + \frac{1}{L}\right\}$$

$\Delta_{II} \Rightarrow \alpha$  : latent hardening (interaction dislocation / dislocation)

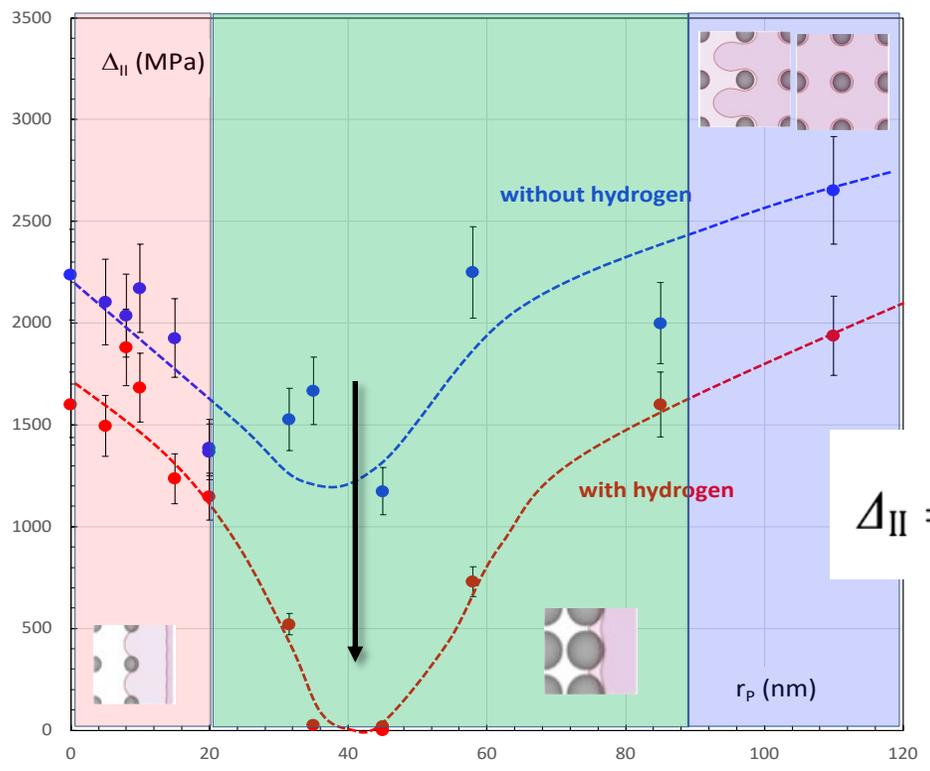
$(\sigma\theta)_0 \Rightarrow L$  : a dislocation length path (imposed by dislocation pattern, GBs and/or twins)

Post-Doc S.P. Murugan  
(2022-2023)

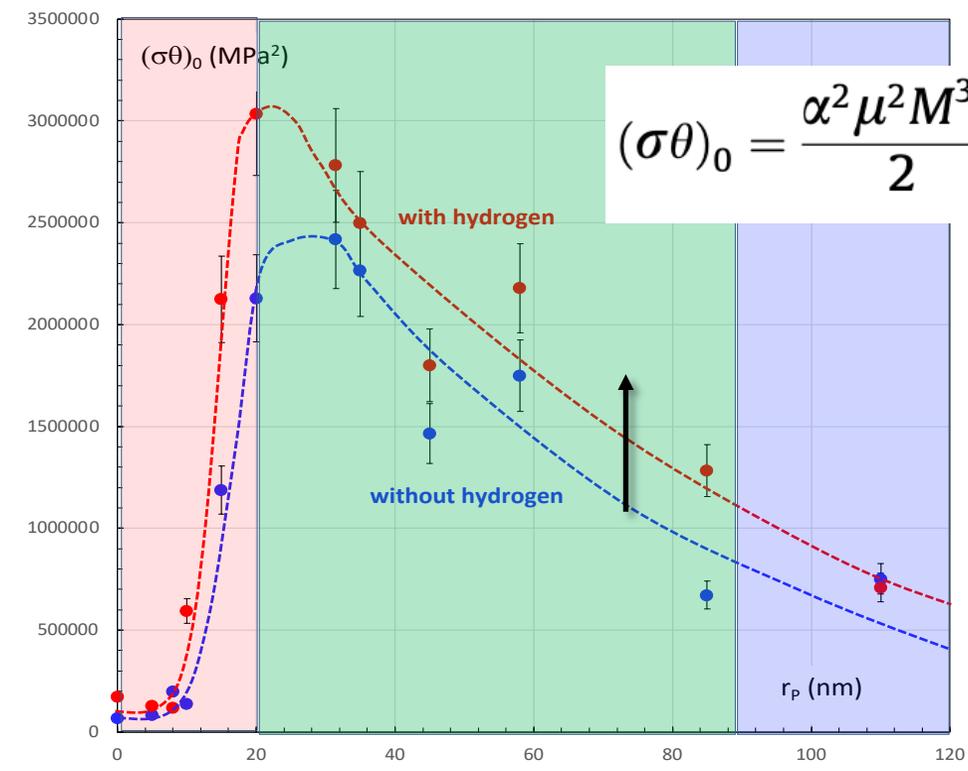
### Kocks-Mecking model

$\Delta_{II} \Rightarrow \alpha$  : latent hardening (interaction dislocation / dislocation)

$(\sigma\theta)_0 \Rightarrow L$  : a dislocation length path (imposed by dislocation pattern, GBs and/or twins)



$$\Delta_{II} = \frac{\alpha \mu M^2}{2\beta}$$



$$(\sigma\theta)_0 = \frac{\alpha^2 \mu^2 M^3 b}{2} \left\{ \frac{k_g}{d} + \frac{1}{L} \right\}$$

- ✓ H decreases the stress hardening  $\Delta_{II}$
- ✓ Shielding effect (H screening the elastic interactions)  $\mu=f(C_H)$
- ✓ Vacancies contributions ?

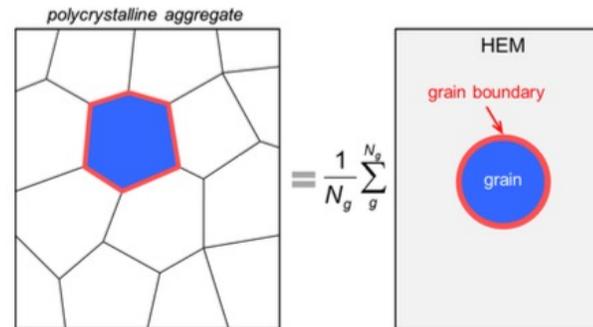
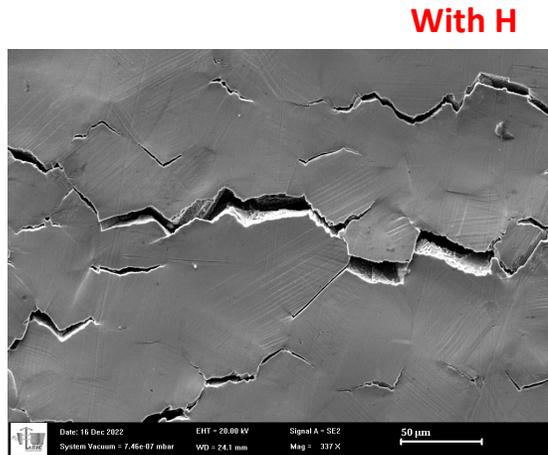
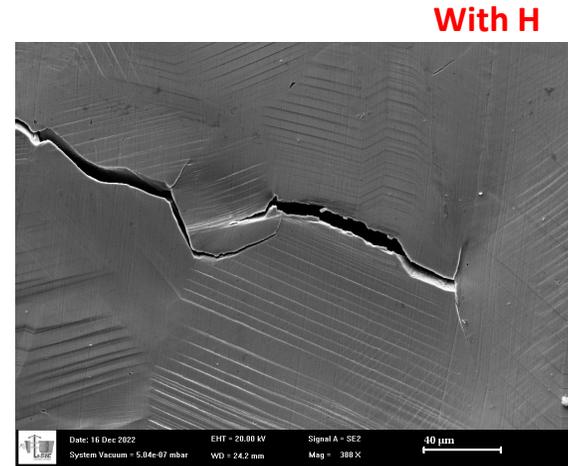
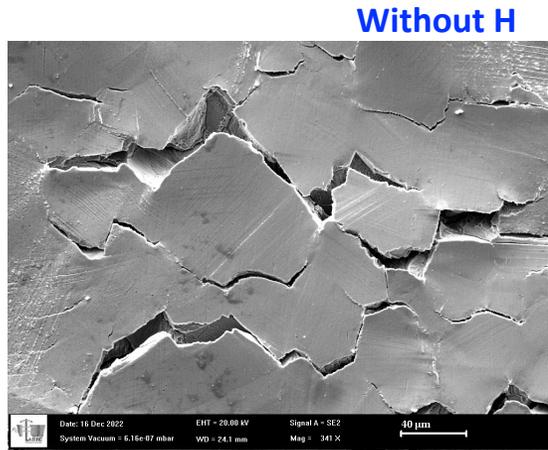
- ✓ H decreases the length path (L) in shearing regimes
- ✓ H increase the length path (L) in Orowan's regime
- ✓ Consequences on intergranular fracture ?

Post-Doc S.P. Murugan (2022-2023)

### Critical stress: $\sigma_c = f(\sigma_m, \epsilon_p)$

Beremin's model [Argon 1976, Beremine 1981, Huez 1998]  
 Based on the Eshelby's inclusion model  
 The grain is described as an inclusion in an average medium

Critical local stress in inclusion until intergranular fracture



$$\sigma_c = \sigma_m + \lambda E_p \epsilon_{eq}^P$$

Hydrostatic stress  $\sigma_m \approx \sigma/3$   
 Form factor  $\lambda \approx 1$  (spherical inclusion)  
 Stress hardening in stage II,  $E_p = \Delta_{II}$   
 Local plastic strain until fracture  $\epsilon_{eq}^P$

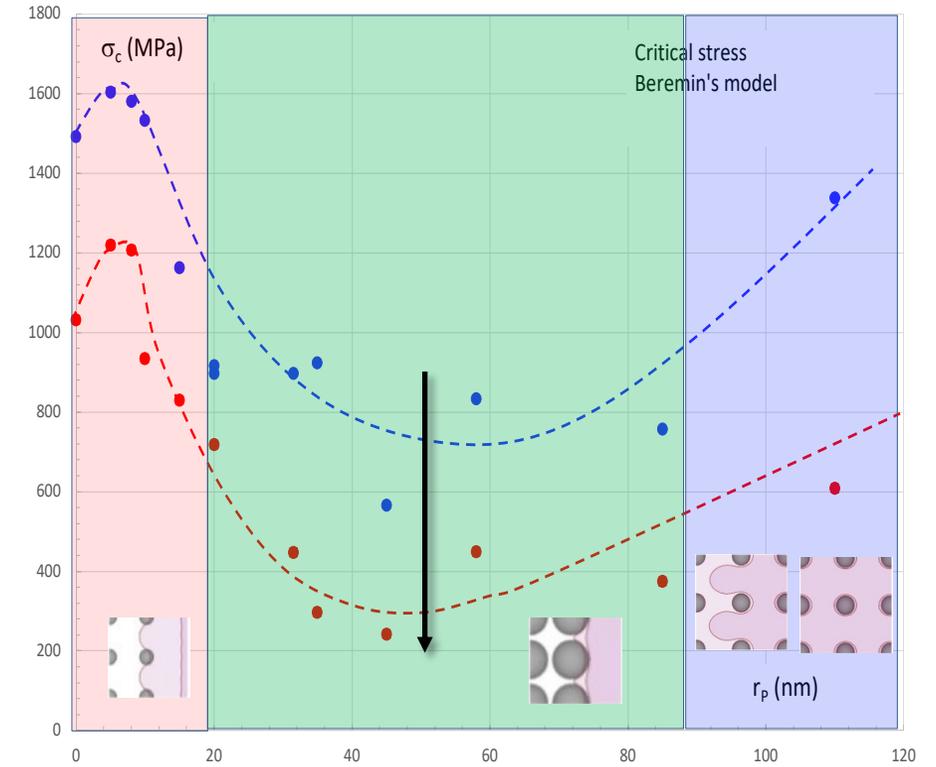
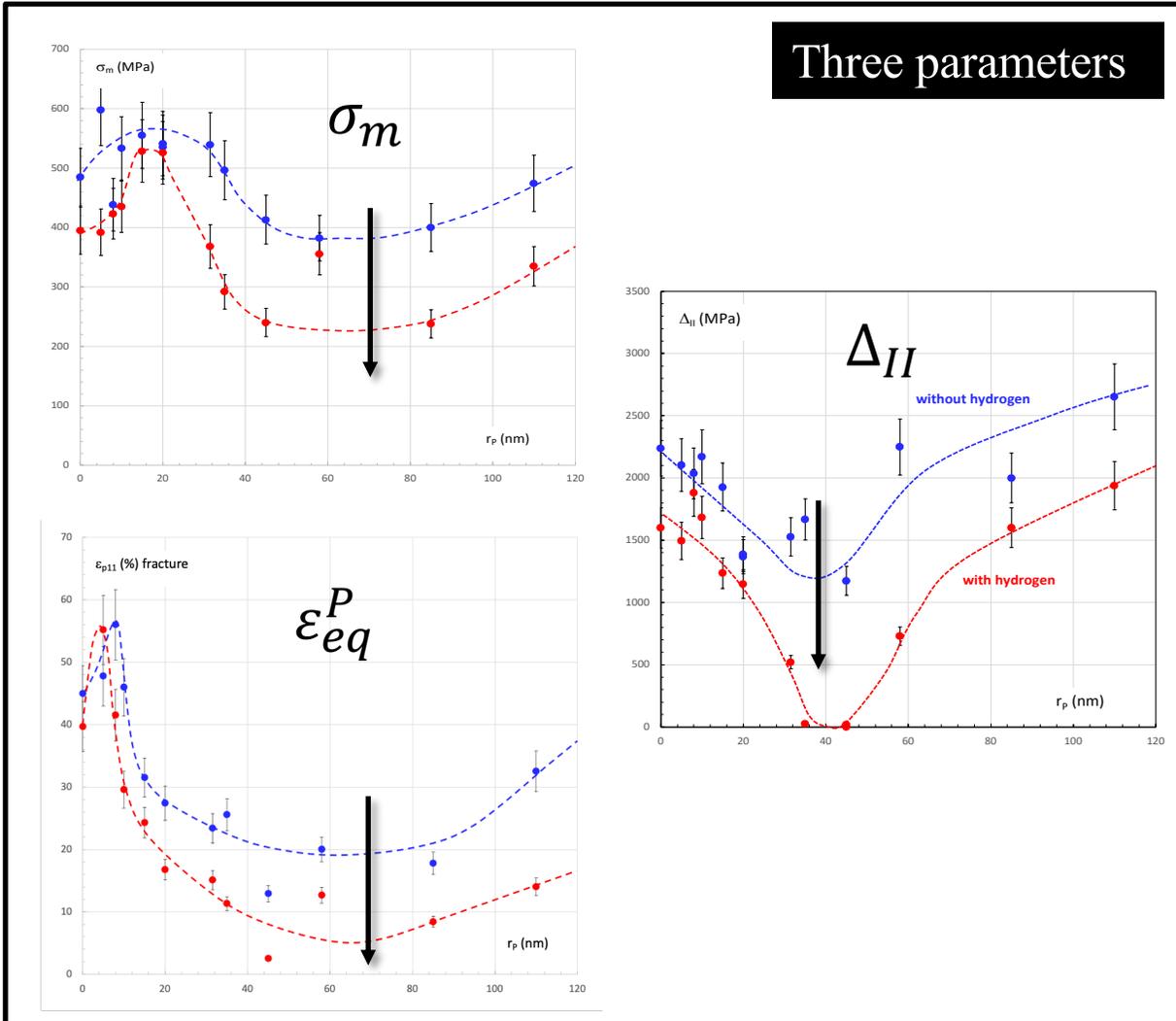
- Simple description : grain in inclusion on Equivalent medium
- Intergranular crack  $\Leftrightarrow$  critical stress at the interface  $s_c$

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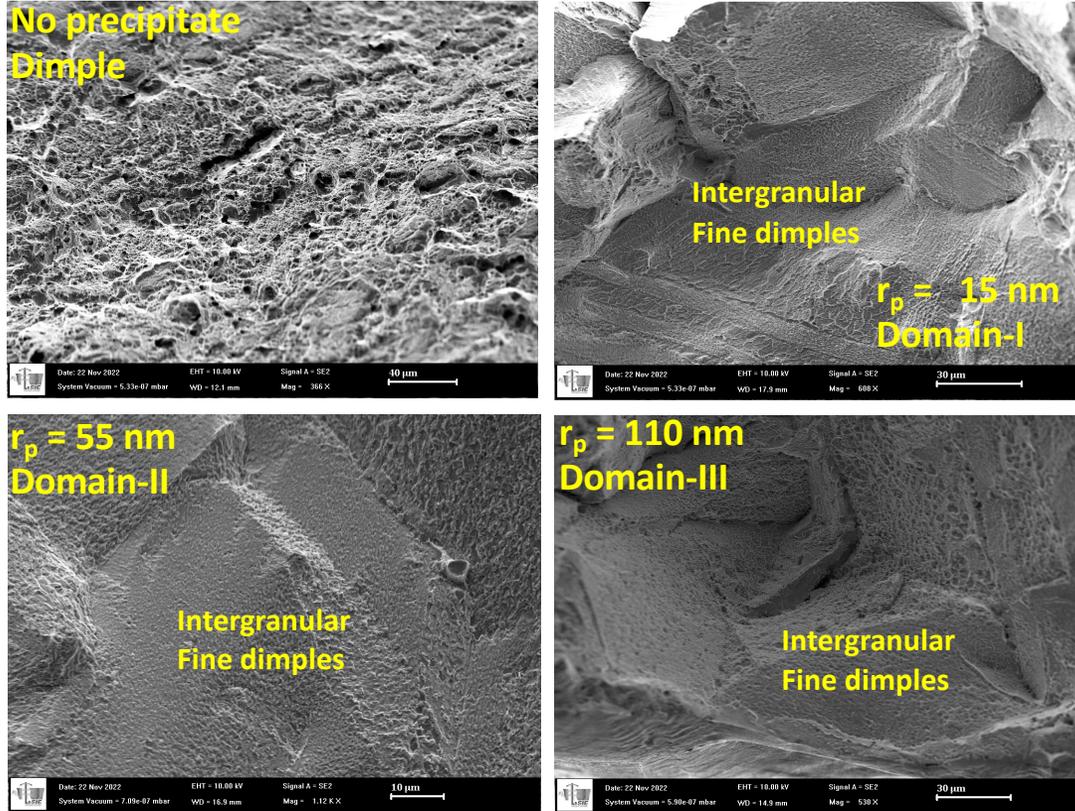
**Critical stress:**  $\sigma_c = \sigma_m + \Delta_{II} \varepsilon_{eq}^P$

### Intergranular fracture



- ✓ H impact stress hardening, ductility, and hydrostatic stress
- ✓ Contribution of the H / plasticity interactions
- ✓ Contribution of H on GBs energy
- ✓ Implication of slip activity and HIC ?

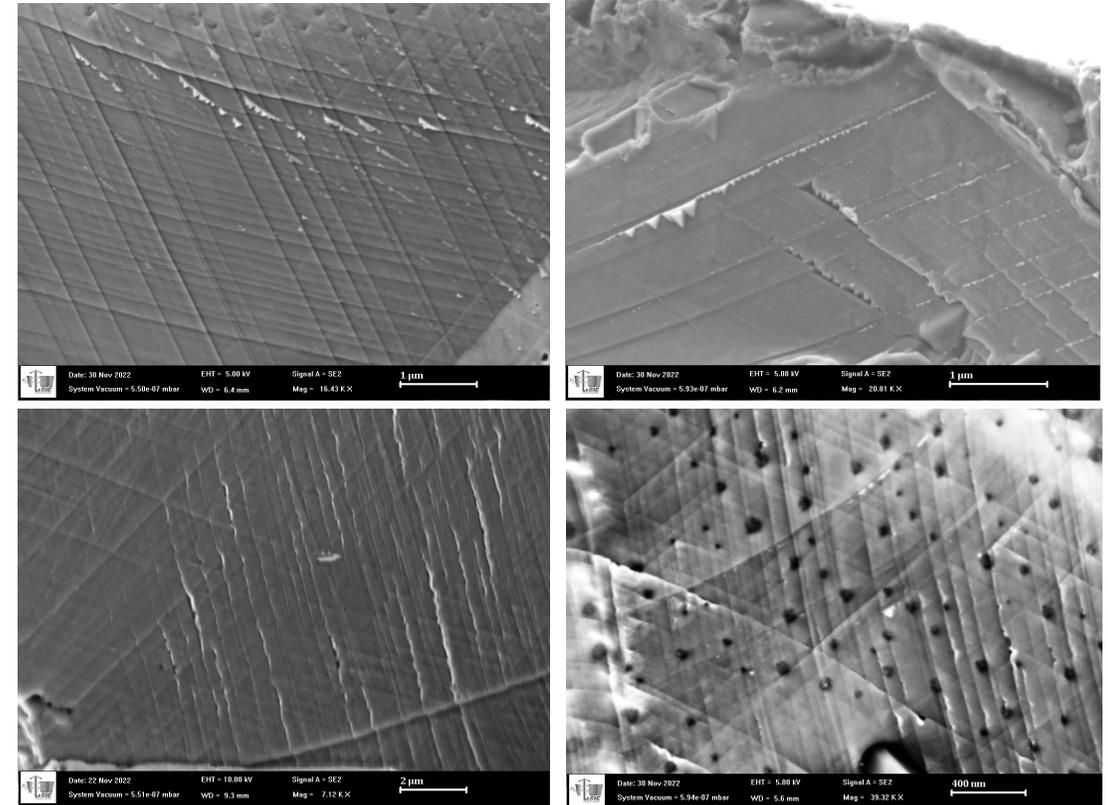
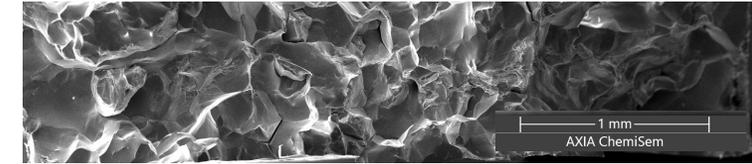
Without H



Precipitate



With H



H promotes plasticity and **vacancies clusters near GBs**

HELP mechanism, Vacancy mechanism

# Conclusion and future challenges

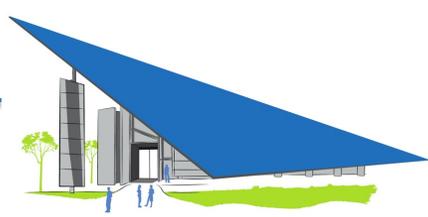
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## Main conclusions

- ❖ Intergranular mechanism of crack depends on hydrogen content/flux, grain-boundary character and slip activity
- ❖ An effective contribution of plasticity and hydrostatic stress on intergranular crack initiation
- ❖ Possible contribution of short circuit of diffusion, GBs network, hydrogen enhances vacancies and dislocation transport of hydrogen
- ❖ Impact on intragranular behaviour need to be improved : dislocation pattern, dislocation localisation, precipitation state, ...
- ❖ Hydrogen enhances the vacancies formation (SAV), Hydrogen enhanced strain-induced vacancy, hydrogen enhances dislocation nucleation and mobility

## Future challenges

- ❖ Hydrogen behaviour near surface : nano-indentation
- ❖ Hydrogen / dislocation interactions *versus* intergranular fracture: length scales
- ❖ Hydrogen implication in crack initiation in fatigue
- ❖ Grain boundaries design versus H: triple junction and additive manufacturing design



*Thanks for your attention*

