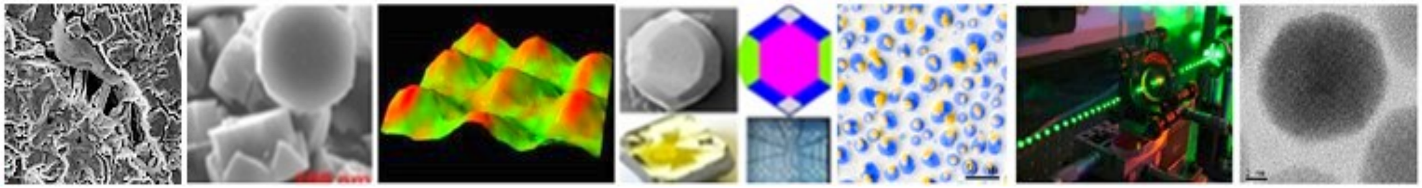


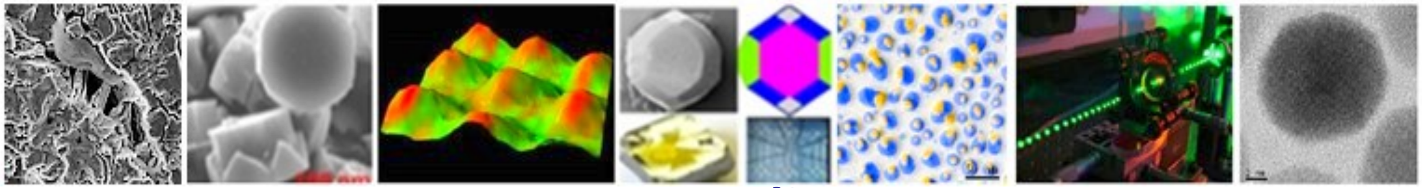
# Metal-Microwave Plasma interaction for Hydrogen Storage

*First evidence of the Ni hydride formation in low temperature Ar/$H_2$-plasma*


M. Redolfi[1], S. Haj-Khlifa[1,2], J. Mougenot[1], Y. Charles[1], M. Seydou[2] and S. Ammar[2]

1 UNIVERSITÉ PARIS 13 LSPM

2 université PARIS DIDEROT PARIS 7 ITODYS



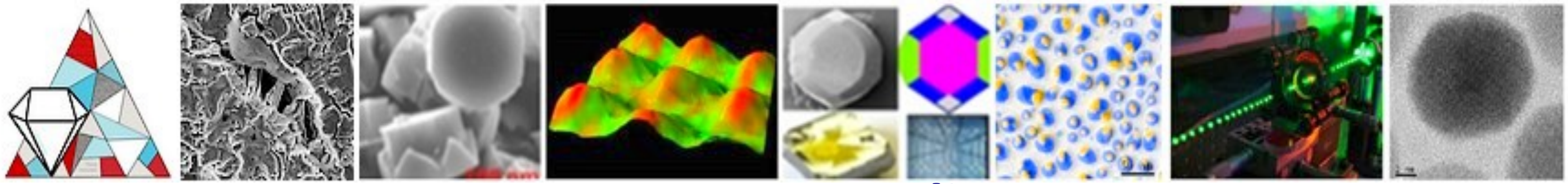
# Outline

1- Objectives and innovative feature of the work

2- Nickel nanopowders synthesis

3- Preliminary results : Hydrogen implantation in Ni pellet

4- Summary and Perspectives



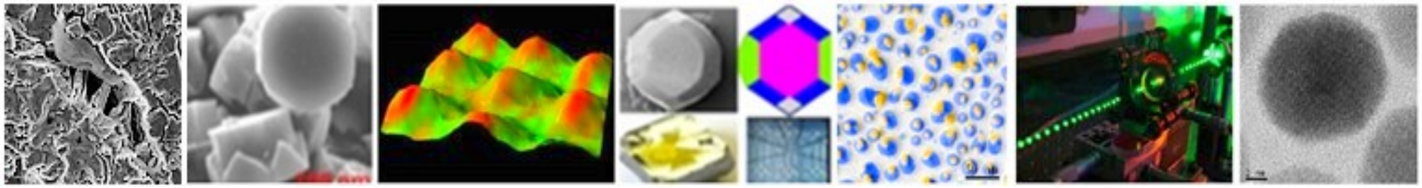
# Outline

## 1- Objectives and innovative feature of the work

## 2- Nickel nanopowders synthesis

## 3- Preliminary results : Hydrogen implantation

## 4- Summary and Perspectives



# Objectives and innovative feature of the work

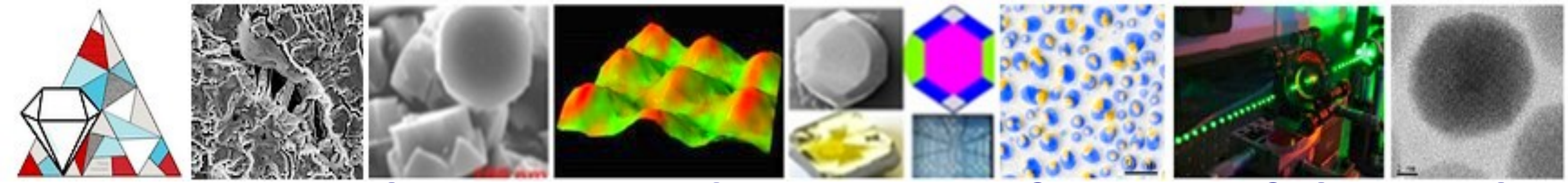
➔ Proof of concept for efficient, fast and reversible cyclic hydrogen storage
➔ Ambient conditions
➔ MW plasma process : H-ions/metal interaction

➔ Storage in the solid state chemical routes (metal hydrides):
- ➔ Higher volume density
- ➔ Higher security

| | Volume density ($g.L^{-1}$) | Mass density (w%) |
|---|---|---|
| **$H_2$ gaz (700 bars)** | 62 | 100 |
| **$H_2$ liquide** | 71 | 100 |
| **$LaNi_5H_6$** | 123 | 1,4 |
| **$TiVCrH_x$** | 205 | 3,5 |
| **$MgH_2$** | 106 | 7,6 |
| **$LiBH_4$** | 122 | 18,3 |

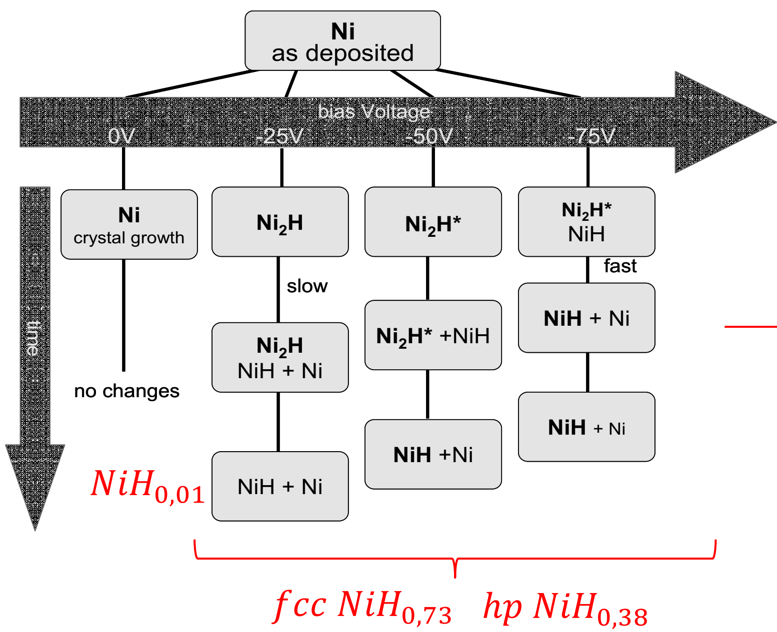
➔ Nickel :
- ➔ Not used for high pressure process (> 0.5 Gpa)
- ➔ Hydrides near to atm : hydrogen plasma
- ➔ Abundant, cheap metal

*P. De Rango et Al., Techniques de l'Ingénieur IN170 (2013)*
*R. Zacharia et Al., J. Nanomaterials (2015)*



# Objectives and innovative feature of the work

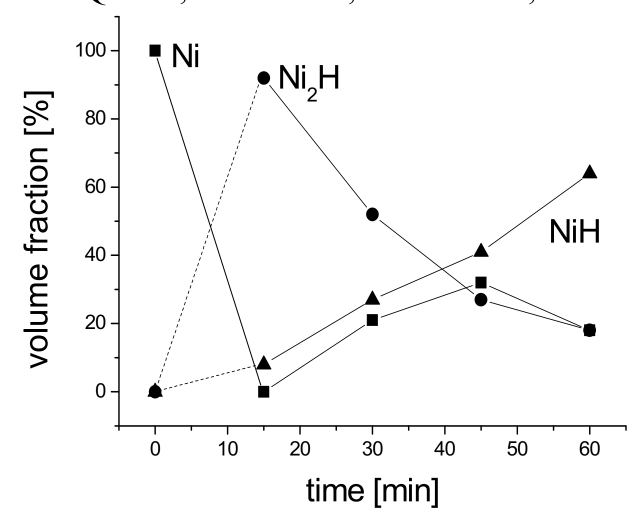
| MW (GHz) | Pu (W) | P (Pa) | $V_{sub}$ (V) | $T_{sub}$ (°C) |
|---|---|---|---|---|
| 2.45 | 700 | 50 | 0 à -100 | 177 |



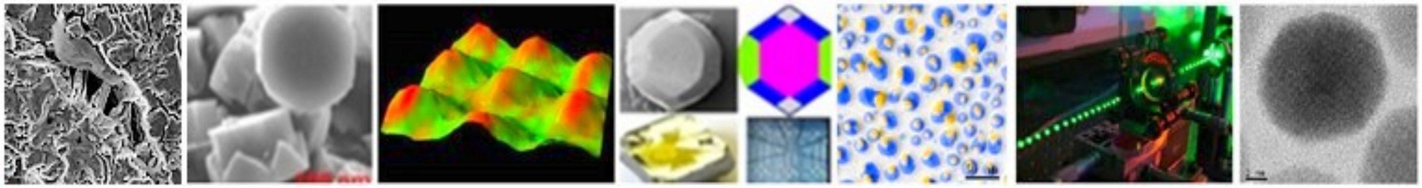

Z. Kristallogr. Suppl. **30** (2009) 241-246 / **DOI** 10.1524/zksu.2009.0035 241


## Formation of nickel hydrides in reactive plasmas

M. Quaas[1], H. Wulff[1,*], O. Ivanova[2], C. A. Helm[2]




- ➔ Previous study : 20 nm thick nickel films
- ➔ Our objective : Nickel pellet (store large amount of H)
- ➔ Difficulty of bulk material : Traps density and H diffusion in volume



# Objectives and innovative feature of the work

Ni Nanopowders

Compaction

Sintering

Ni pellet with nanograins.
Densification <50%

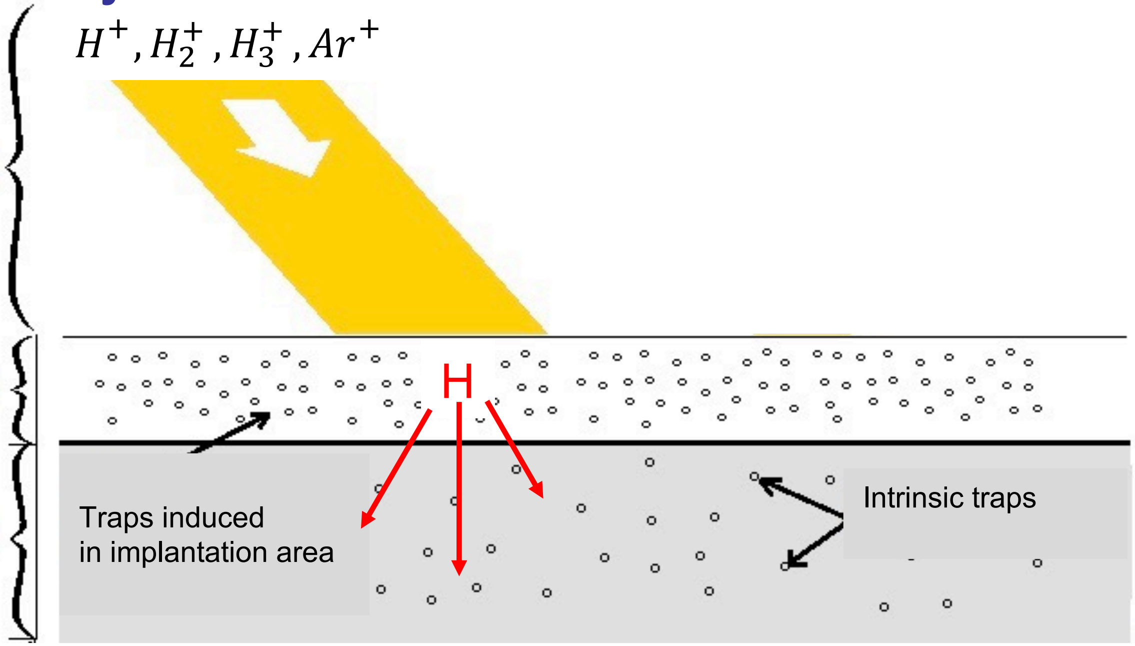
Ni pellet with nanograins.
Densification : 87%

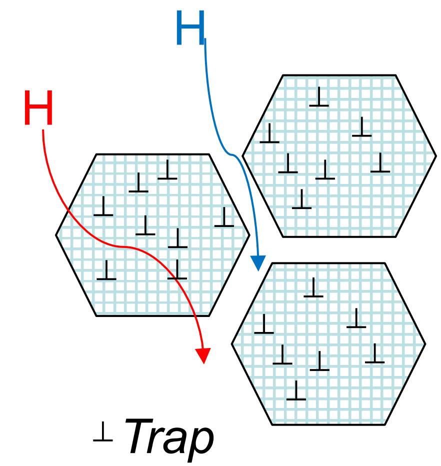
High specific surface
Mecanically unsteady (crumbly)

Mecanically steady
Risk of grain size enlargement

# Objectives and innovative feature of the work

## Nanopowders sintered

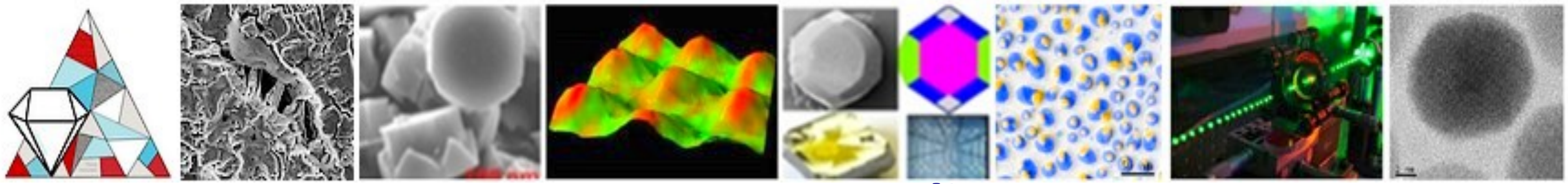



➔ H diffusion : interstitials sites + GB + Triple junction
➔ H traps: interstitials sites + intrinsic traps

## Nanopowders compacted

➔ H diffusion : interstitials sites + pores (no GB)
➔ H traps: interstitials sites + vacancies



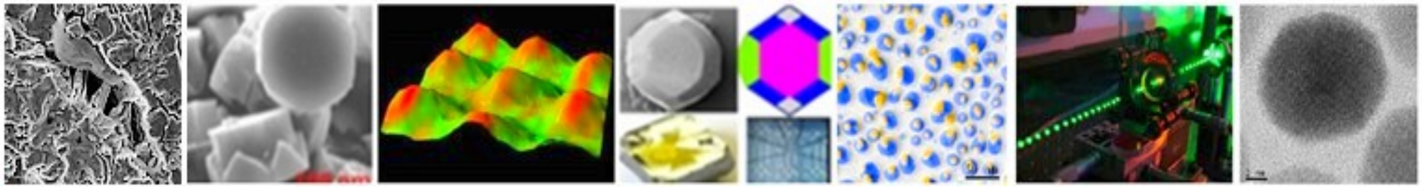
# Outline

1- Objectives and innovative feature of the work

**2- Nickel nanopowders synthesis**

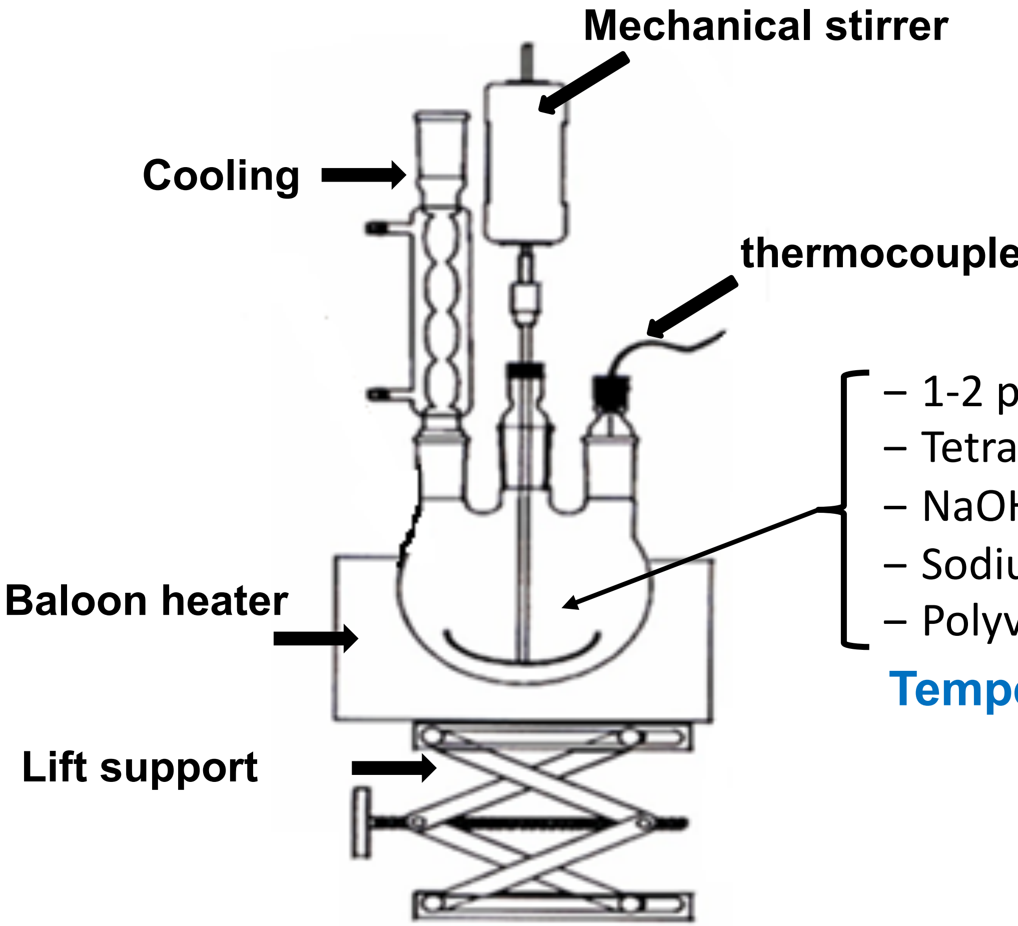
3- Preliminary results : Hydrogen implantation

4- Summary and Perspectives



# Nickel nanopowders synthesis : Polyol process

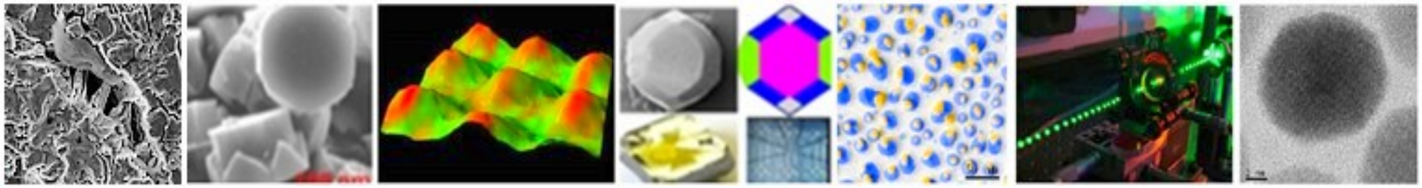
- **High crystalline quality**
- **Aggregation degree control**
- **Shape control**
- **Size control**



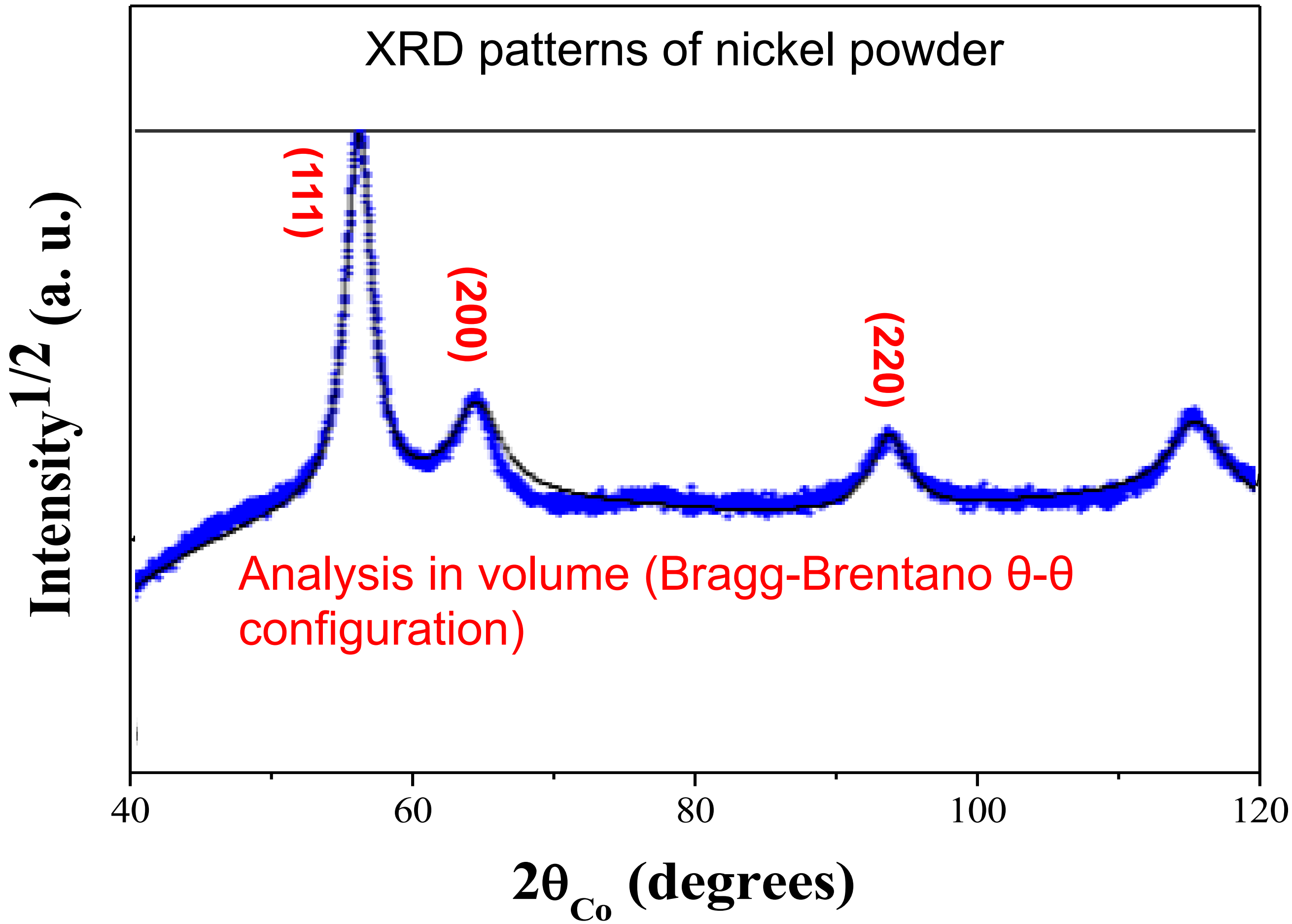

- 1-2 propandiol (reducing power)
- Tetrahydrated Nickel acetate (precursor)
- NaOH
- Sodium borohydride (reducing additive)
- Polyvinylpyrrolidone (dispersing additive)

**Temperature :** 180°C ( 10°C/mn)

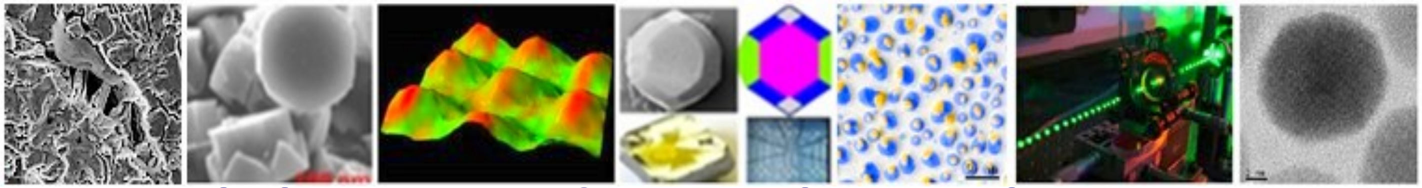
*M. Srisudha et al., Nano Vision 37 (2012) 37*
*K.J. Carroll et al., J. Phys. Chem. C 115 (2011) 2656*



# Nickel nanopowders synthesis : characterization

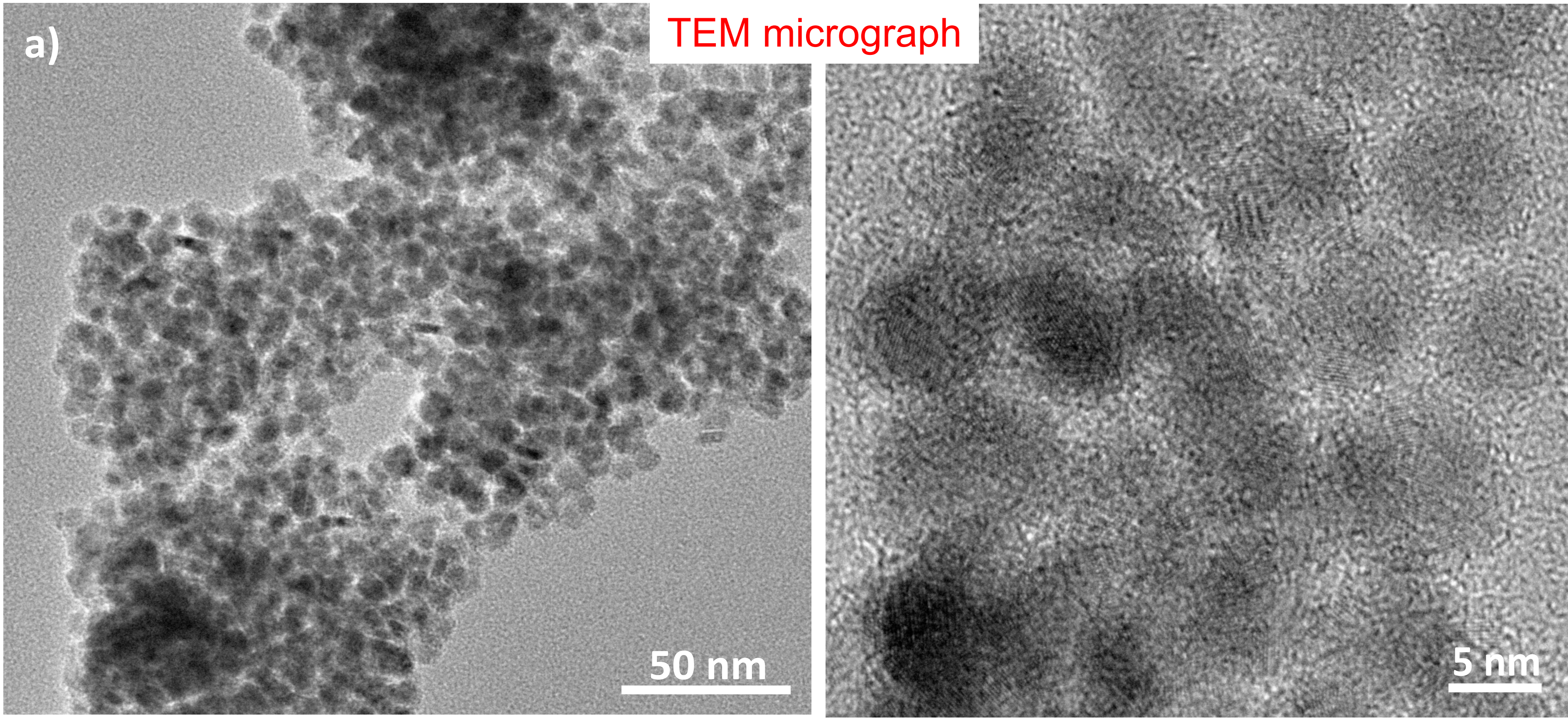



Rietveld refinement analyze : fcc nickel (ICDD n°98-004-3397) a = 3.531
Scherrer crystallites average size : 3 nm.

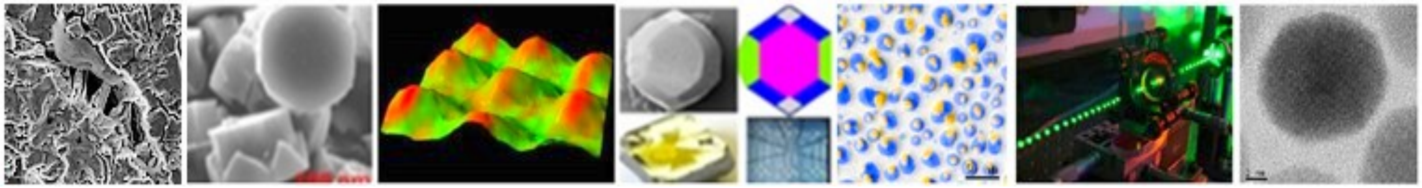


# Nickel nanopowders synthesis : characterization

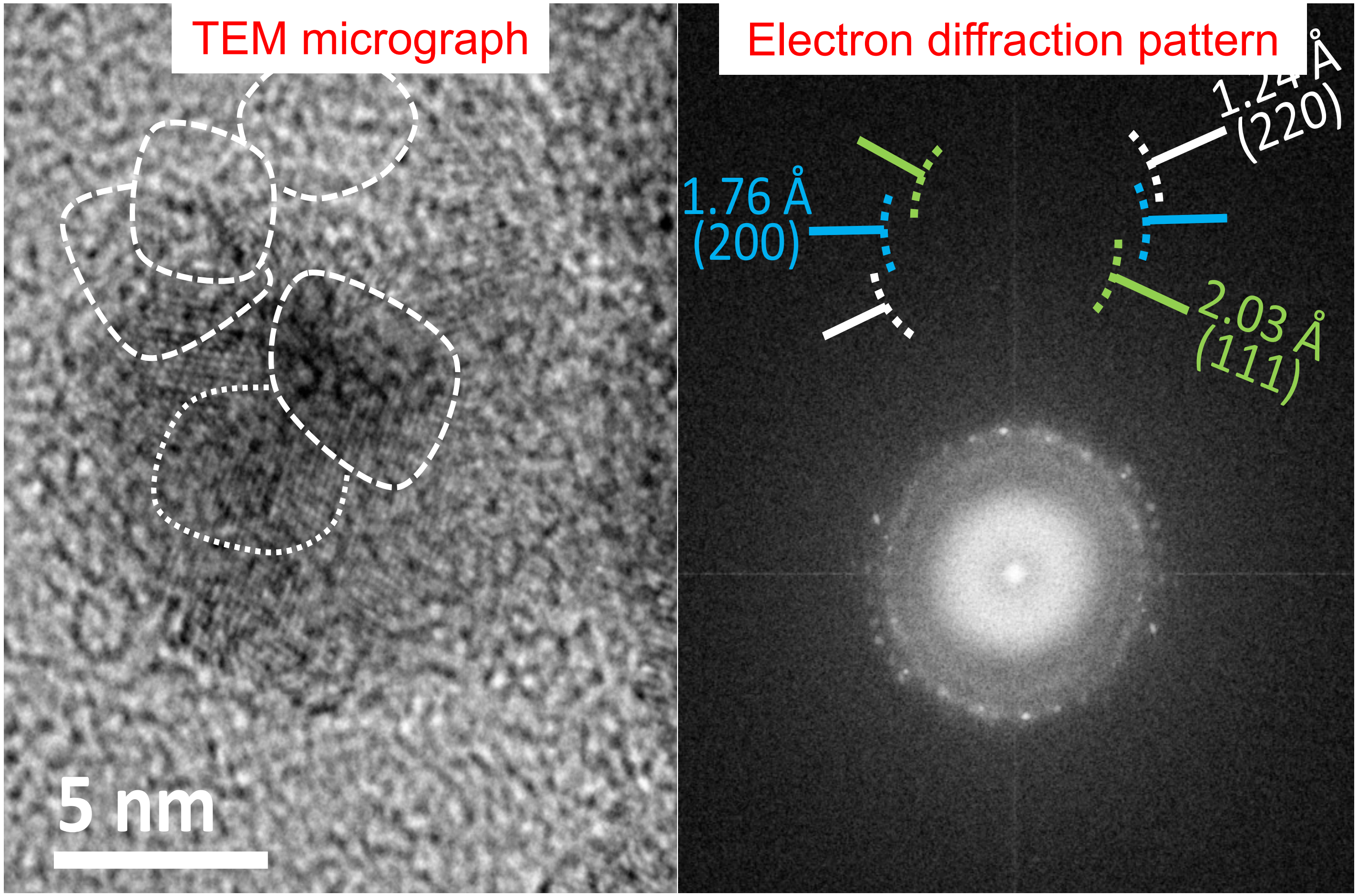
TEM micrograph




➔Average particle diameter : 8 nm
➔HRTEM FFT analysis : isotropic in shape polycrystalline particles

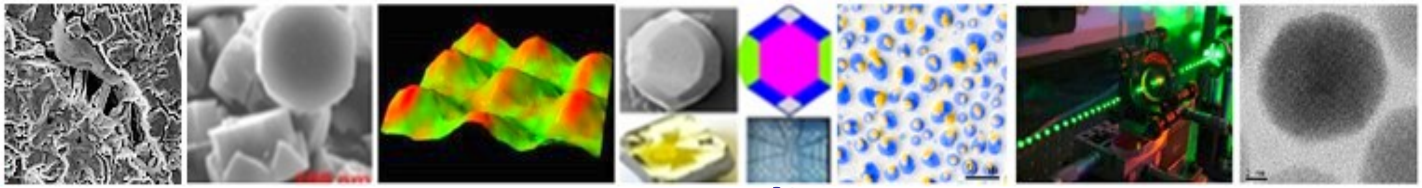


# Nickel nanopowders synthesis : characterization




➔Primary particles : 3 nm

➔(hkl) reticular distances of pure *fcc* Ni



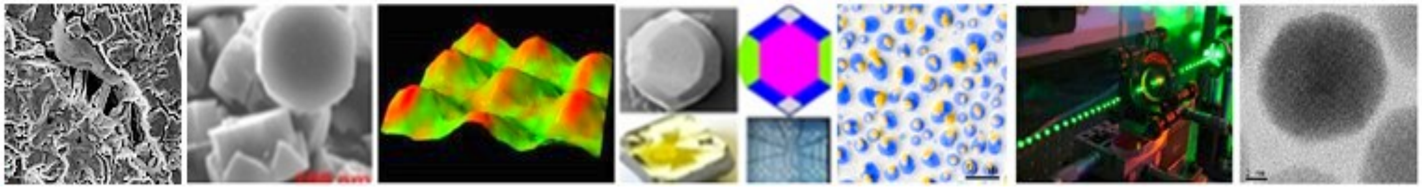
# Outline

1- Objectives and innovative feature of the work

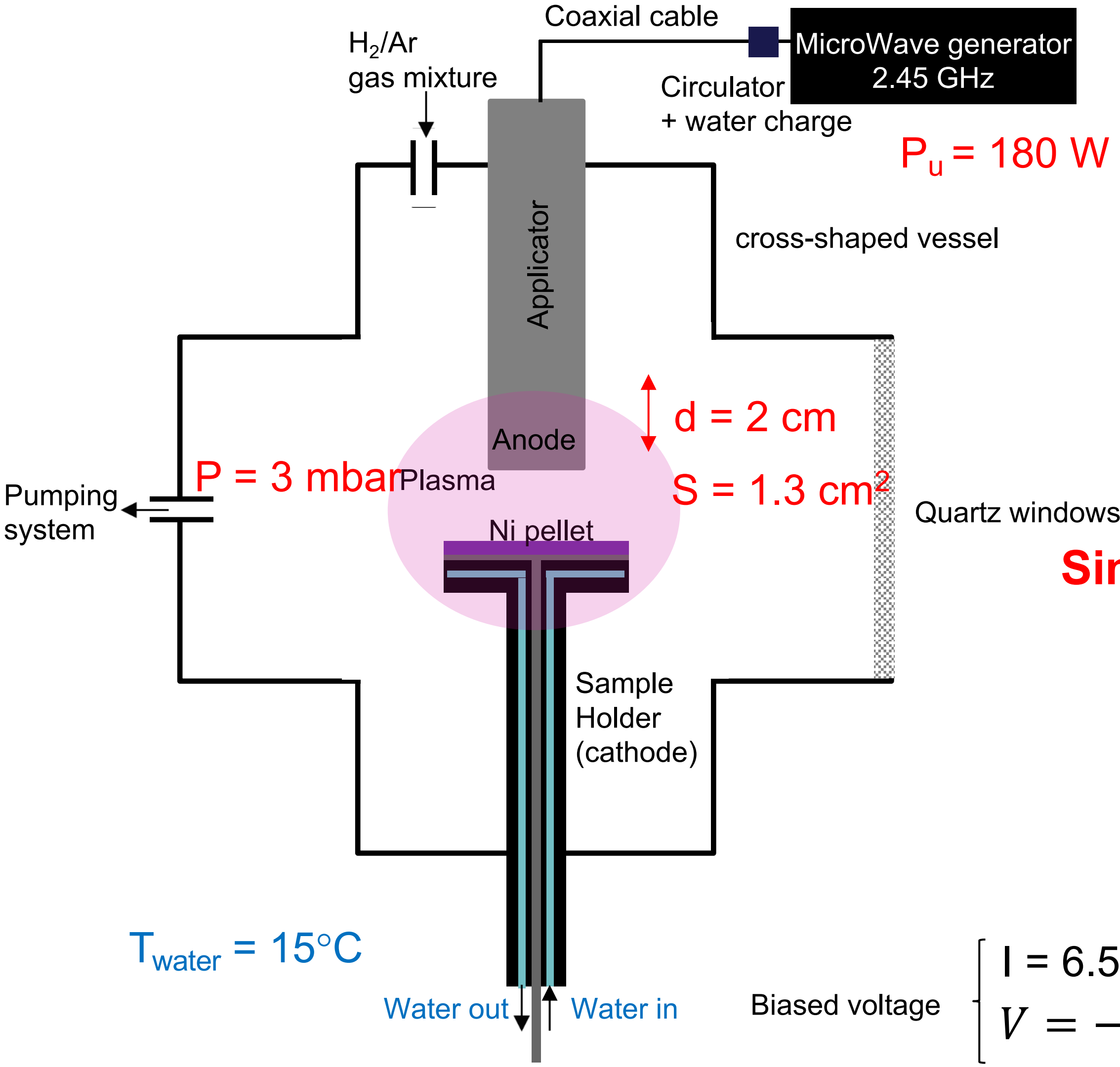
2- Nickel nanopowders synthesis

**3- Preliminary results : Hydrogen implantation**

4- Summary and Perspectives



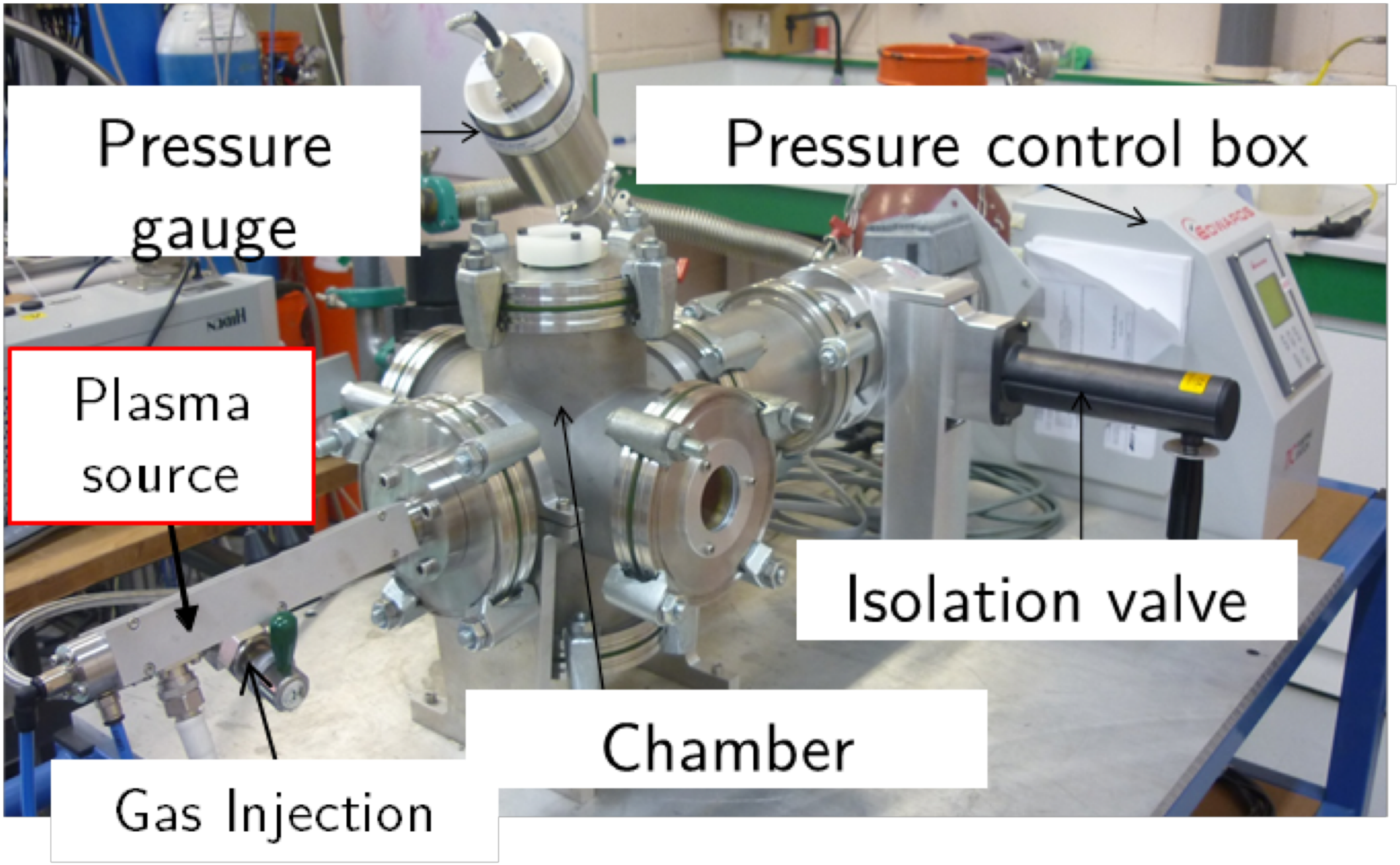
# Preliminary results : H implantation in compacted nanopowders

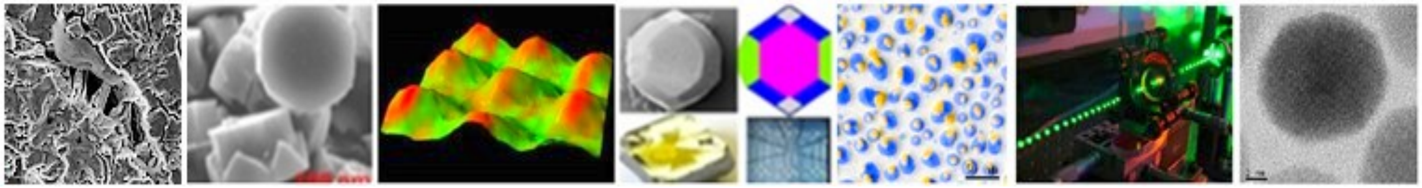



**Similar to Plasma Immersion Ion Implantation process**

Biased voltage
$$\begin{cases} I = 6.5\ \text{mA} \longrightarrow \boxed{\Gamma = 3.1\times10^{20} H.m^{-2}.s^{-1}} \\ V = -50V, E_{ions} = 50\ eV \end{cases}$$

# Preliminary results : H implantation in compacted nanopowders





# Preliminary results : H implantation in compacted nanopowders

$$Why\ E_{ions} = 50\ eV\ ?$$

$\longrightarrow E_{ions}(eV)$

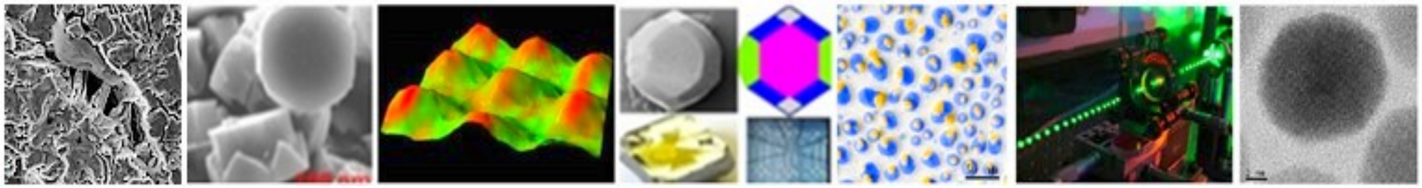
| Implantation | Implantation<br>Sputtering | Implantation<br>Sputtering<br>Defects (vacancies) |
|---|---|---|

$$E_{sput} = \frac{(M_{ion} + M_{Ni})^2 E_{sublim}}{4M_{ion} \times M_{Ni}}$$

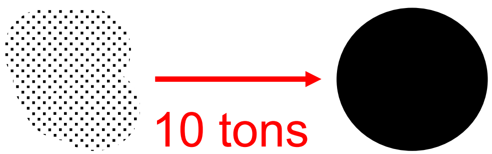
$$E_{def} = \frac{(M_{ion} + M_{Ni})^2 E_{displac}}{4M_{ion} \times M_{Ni}}$$

| | $E_{sput}$ (eV) | $E_{def}$ (eV) |
|---|---|---|
| $Ni/H^+$ | 52 | 519 |
| $Ni/H_3^+$ | 19 | 185 |
| $Ni/Ar^+$ | 4 | 36 |

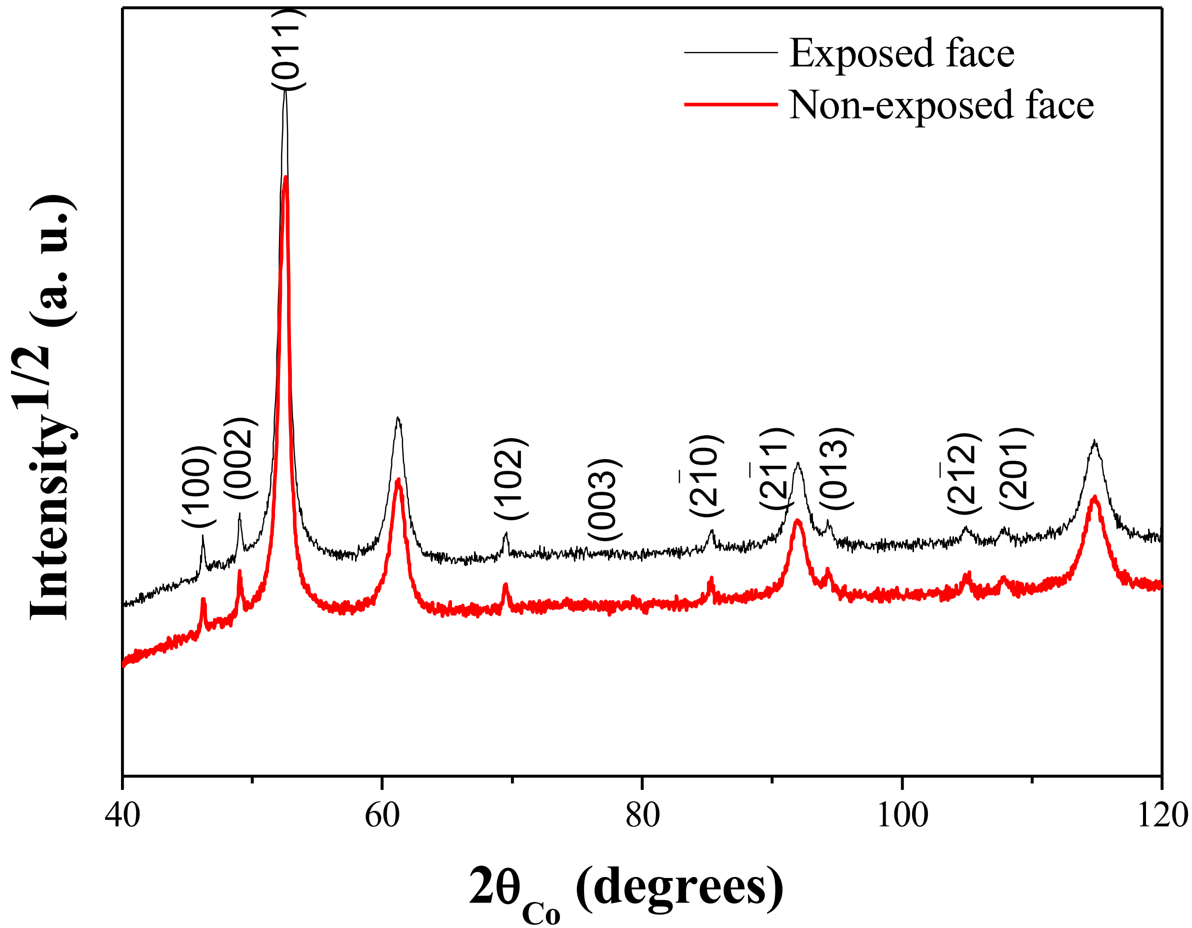
➔ Intrinsic traps + additional traps with $Ar^+$



# Preliminary results : H implantation in compacted nanopowders



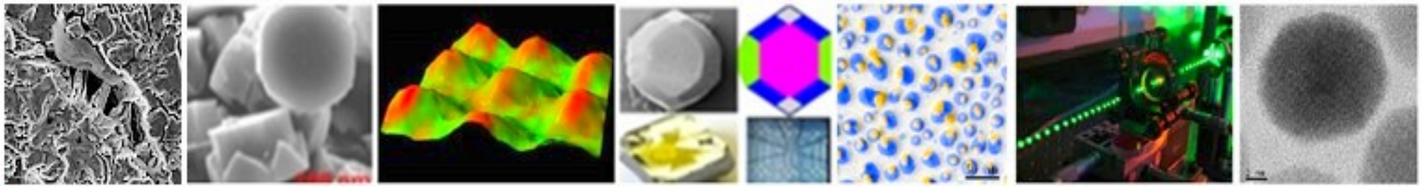

- MW power : 180 W
- P = 3 mbar
- Exposition time : 6h
- $\Gamma = 3.1\times10^{20} H.m^{-2}.s^{-1}$




➔ Hexagonal $Ni_2H$ structure (ICDD n° 98-020-0593) in volume.

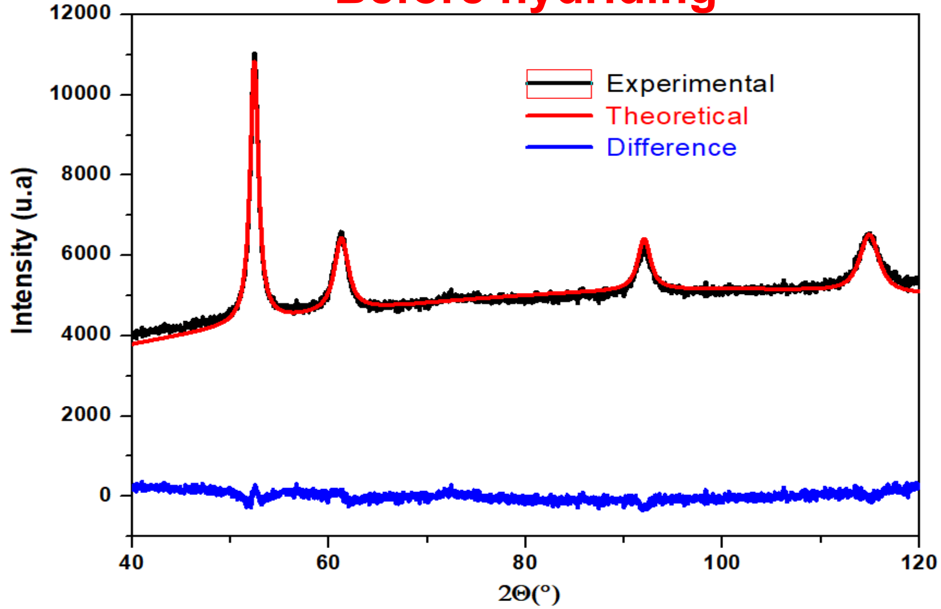
$$2Ni + H \rightarrow Ni_2H$$

$$Ni_2H \rightarrow NiH + Ni$$

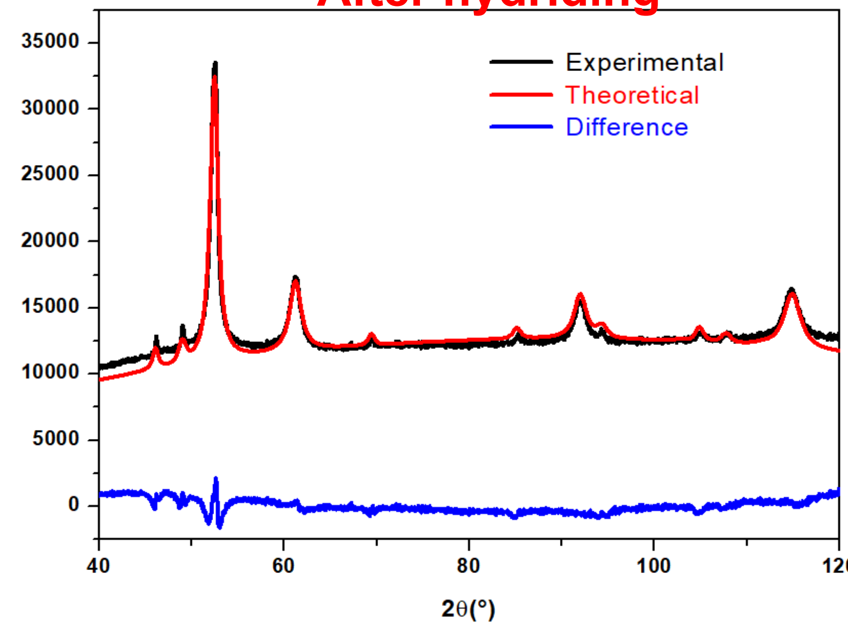


# Preliminary results : H implantation in compacted nanopowders

**Before hydriding**




**After hydriding**




Single-phase material
Well crystallized
Ni fcc

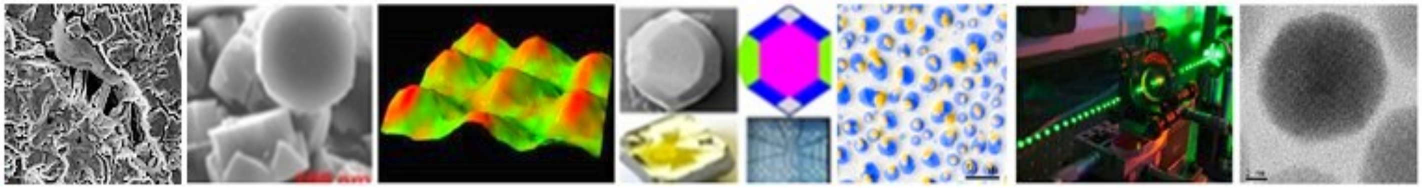
Two-phase material

Ni fcc

w% : 77

$Ni_2H$
Hexagonal

w%: 23



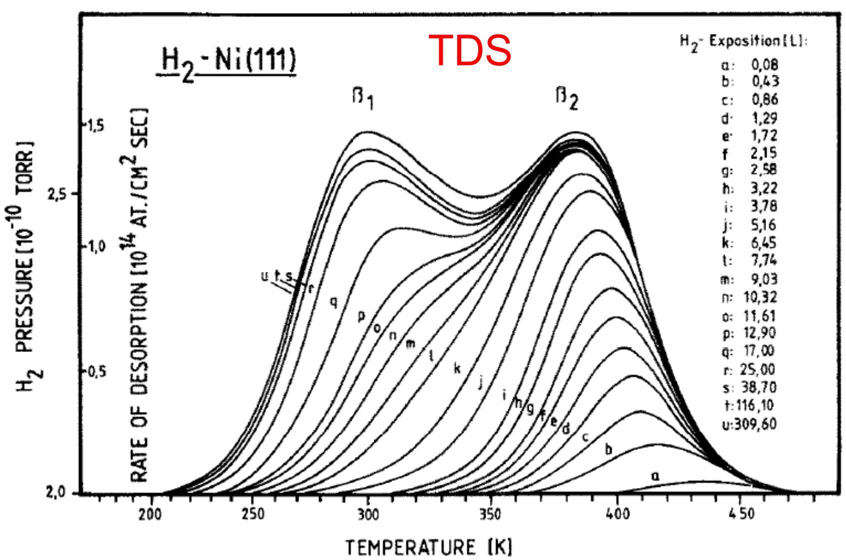
# Preliminary results : H implantation in bulk nickel

- ➔ 1D Model HIIPC (*Hydrogen Isotopes Inventory Processes Code*)
- ➔ H diffusion in pores and GB not taken into account
- ➔ Coupled kinetic equations solved by finite differences

$$\Gamma = (1-R)\Gamma_0\varphi(z)$$

$$\begin{cases} \dfrac{\partial C_s(z,t)}{\partial t} = D\partial \dfrac{\left[\dfrac{\partial C_s(z,t)}{\partial z}\right]}{\partial z} + \Gamma(z,t) - \sum_i \dfrac{\partial C_t^i(z,t)}{\partial t} \\ \dfrac{\partial C_t^i(z,t)}{\partial t} = v_t^i\left[1-\dfrac{C_t^i(z,t)}{n_{trap}}\right]C_s(z,t) - v_d^i C_t^i(z,t) \end{cases}$$

Bibliographical data



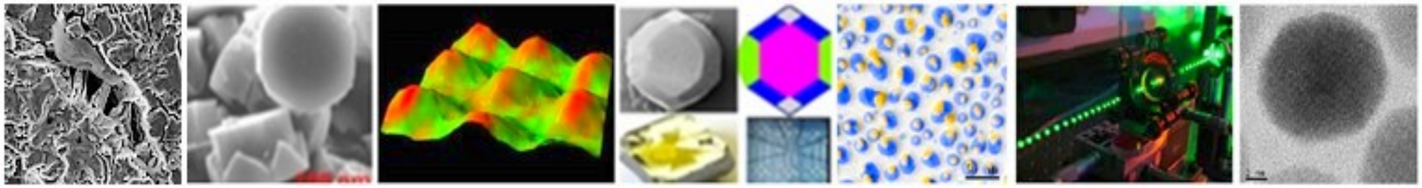

| $D_0$ $(m^2/s)$ | $E_D$(eV) | $E_{Traps}$ (eV) | Traps density |
|---|---|---|---|
| $6.4\times10^{-7}$ | 0.42 | 0.997 ($\beta_1$)<br>0.867 ($\beta_2$) | 0,09510$^{-3}$ ($\beta_1$)<br>0,15.10$^{-3}$ ($\beta_2$) |

$D_{Lattice}$

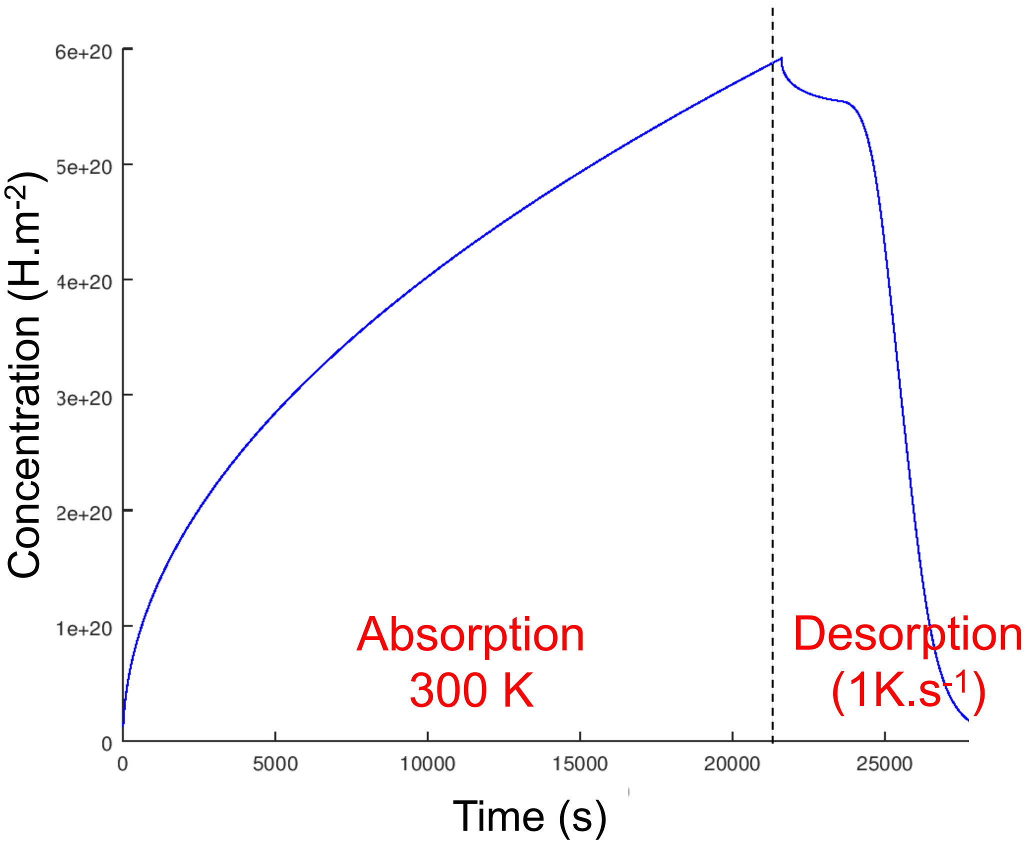
Vacancies + dislocations

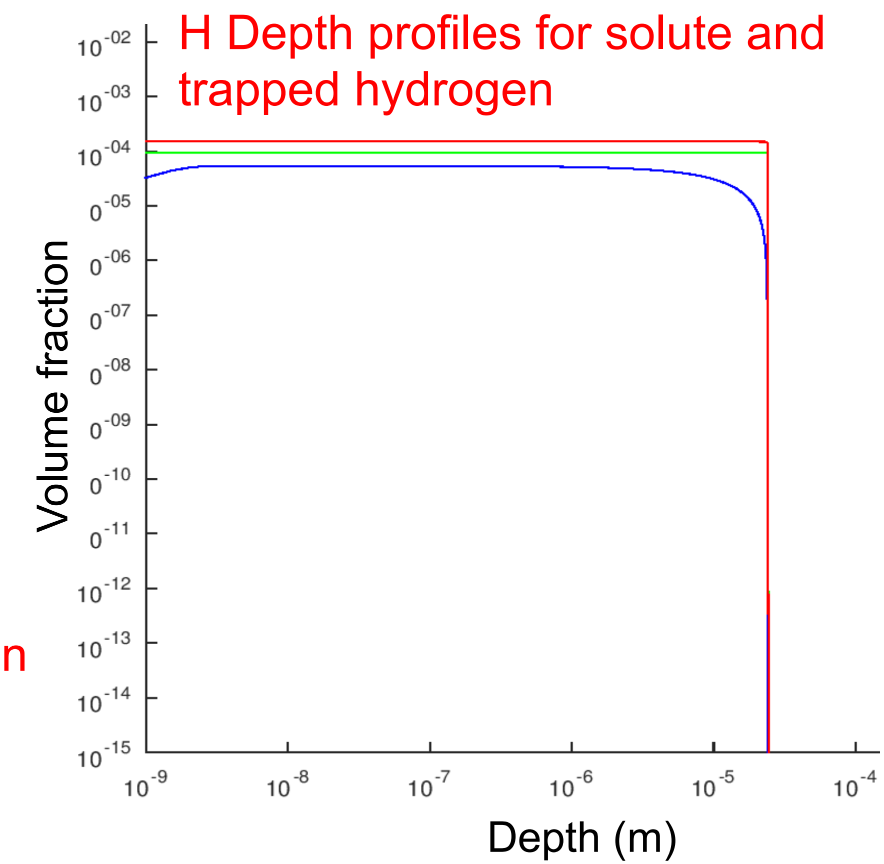
$$D = D_0\exp\left(\frac{-E_D}{kT}\right)$$


*S. Chaofeng et al., Nuclear Fusion 52 (2012) 043003.*
*A. McNabb et al., Trans. Metallurgical Soc. AIME 227 (1963) 618.*
*A.Winkler et al., Surface science 118 (1982) 19.*

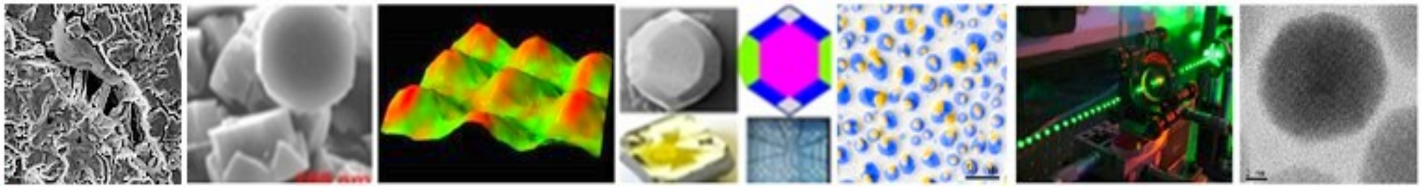


# Preliminary results : H implantation in bulk nickel

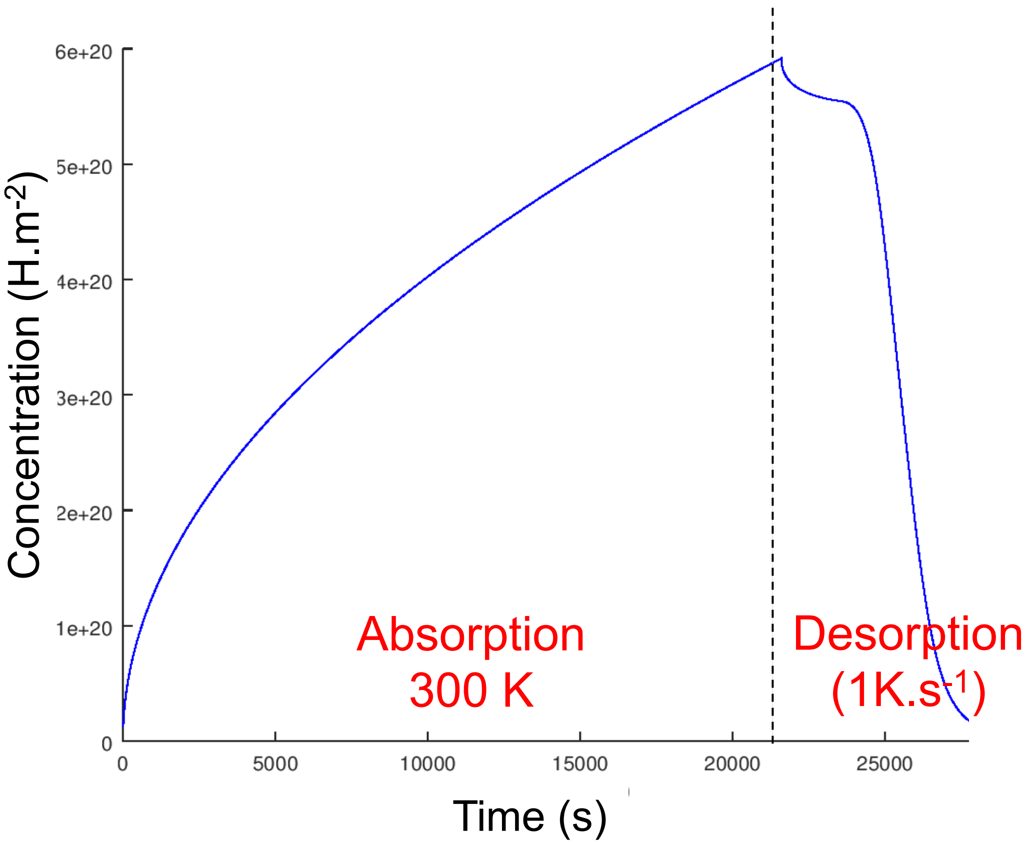


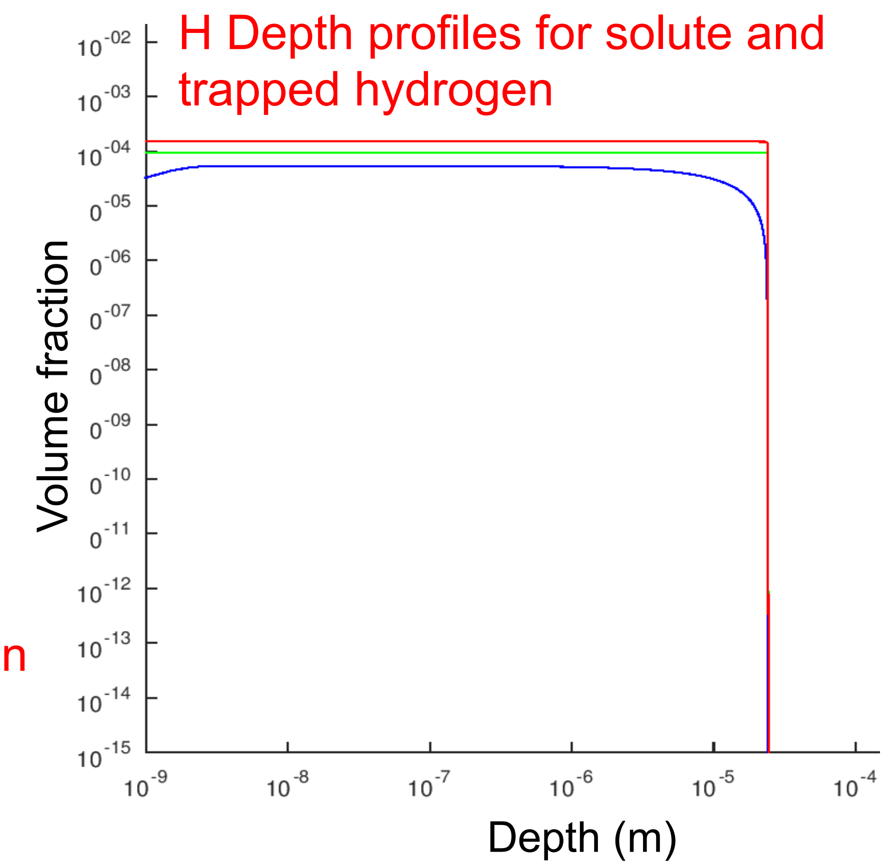




➔ Feasibility to store hydrogen in volume at low temperature by MW plasma



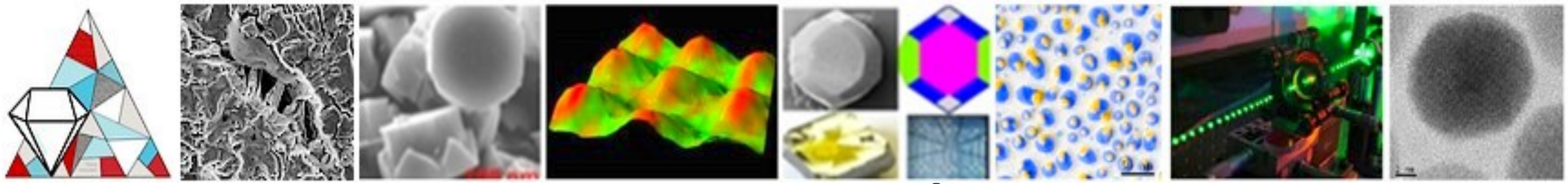
# Preliminary results : H implantation in bulk nickel




➔ H desorption at low heating

➔ Highlights of the reversible hydrogen storage near to ambient conditions



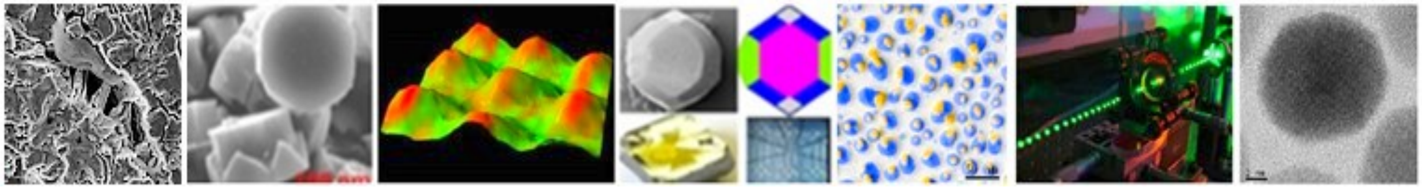
# Outline

1- Objectives and innovative feature of the work

2- Nickel nanopowders synthesis

3- Preliminary results : Hydrogen implantation

**4- Summary and Perspectives**

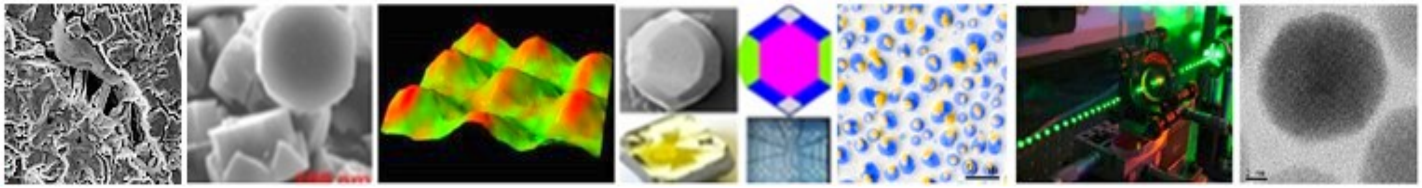


## Summary

- ➔ Synthesis of compacted Ni pellet with nanograins
- ➔ Experimental evidence of the Ni hydrides formation
- ➔ Numerical evidence of hydrogen volume storage at low temperature
- ➔ Hydrogen desorption possibility at low heating : cyclic hydrogen storage near to ambient conditions

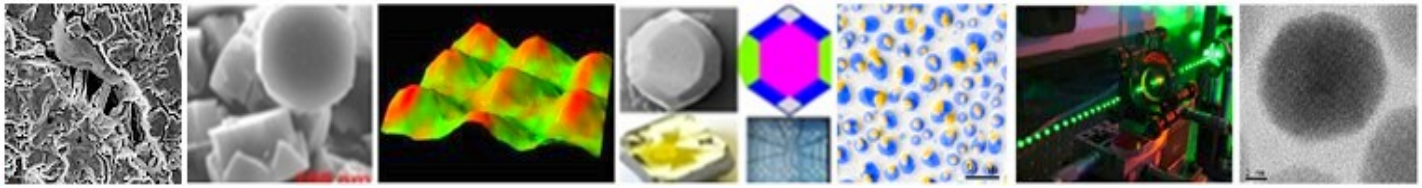
## Perspectives

- ➔ Thermal Desorption Spectroscopy to determine hydrogen stored and traps energies
- ➔ Experimental and numerical tests in Ni nanopowders sintered
- ➔ Short-circuit diffusion inside grains boundaries and triple junctions
- ➔ Mechanical defects creation to increase trap density



# Promotion / Emulation

- Scientific paper being written. Acknowledgments : *"Financial support through Labex SEAM (Science and Engineering for advanced Materials and Devices), ANR 11 LABX 086, ANR 11 IDEX 05 02.*
- 16th International Conference on Plasma Surface Engineering September 17-21, 2018, Garmisch-Paternkirchen, Germany (Oral)
- SPS 2017 : Journées Nationales sur le Frittage par Courant Pulsé October 5-6, 2017, Villetaneuse, France (Poster)
- "TOMENHY" project. ANR AAP 2019. LSPM – ITODYS – Louis Néel Institute.
- Related project : "A plasma based boost diffusion treatment for titanium oxidation (PLASTIOX)". Projet emergent. LSPM – ITODYS. D. Chaubet, B. Bacroix, M. Redolfi, S. Ammar, F. Mammeri



# LSPM references - Hydrogen absorption by MW plasma


K. Ouaras, M. Redolfi*, D. Vrel, C. Quiros, G. Lombardi, X. Bonnin, and K. Hassouni. 2018. "Tungsten Blister Formation Kinetic as a Function of Fluence, Ion Energy and Grain Orientation Dependence Under Hydrogen Plasma Environment". Journal of Fusion Energy. 37. 144-53

C. Quirós, J. Mougenot, G. Lombardi, M. Redolfi*, O. Brinza, Y. Charles, A. Michau, K. Hassouni. 2017. "Blister formation and hydrogen retention in aluminium and beryllium : A modeling and experimental approach". Nuclear Materials and Energy. 12. 1178-1183

C. Grisolia, E. Hodille, J. Chene, S. Garcia-Argote, G. Pieters, A. El-Kharbachi, F. Jambon, L. Marchetti, F. Martin, F. Miserque, D. Vrel, M. Redolfi*, V. Malard, G. Dinescu, T. Acsente, F. Gensdarmes, S. Peillon, B. Pegourié and B. Rousseau. 2015. "Tritium absorption and desorption in ITER relevant materials : comparative study of tungsten dust and massive samples". Journal of Nuclear Materials. 463. 885-888

A. El-Kharbachi, J. Chêne, S. Garcia-Argote, L. Marchetti, F. Martin, F. Miserque, D. Vrel, M. Redolfi*, V. Malard, C. Grisolia and B. Rousseau. 2014. "Tritium absorption/desorption in ITER-like tungsten particles". International Journal of Hydrogen Energy. 39. 10525-10536



**Orcid ID : 0000-0003-4327-7184 - ResearcherID : E-8684-2012 - Scopus Author ID : 25631531900*