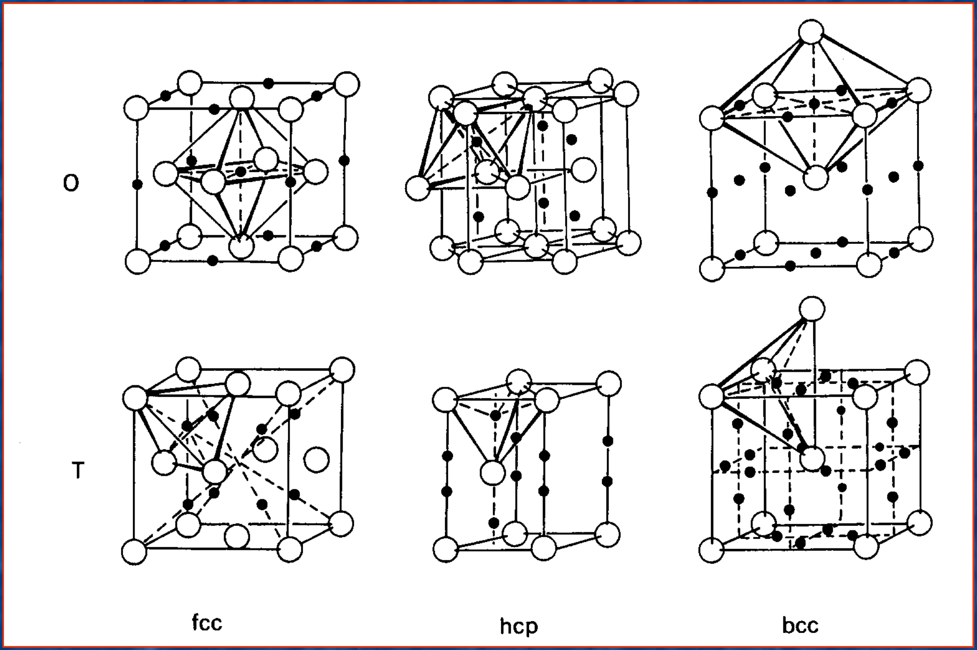
Alternative routes for hydrogenation of metallic species

D. FRUCHART, S. MIRAGLIA
Institut Néel- Grenoble

hydrogen location in metals

- Relevant tool = neutron diffraction
- Interstitial sites
  - Tetrahedral
  - Octahedral



Hydrures Interstitiels
vs Hydrures à Haute Densité de Lacunes

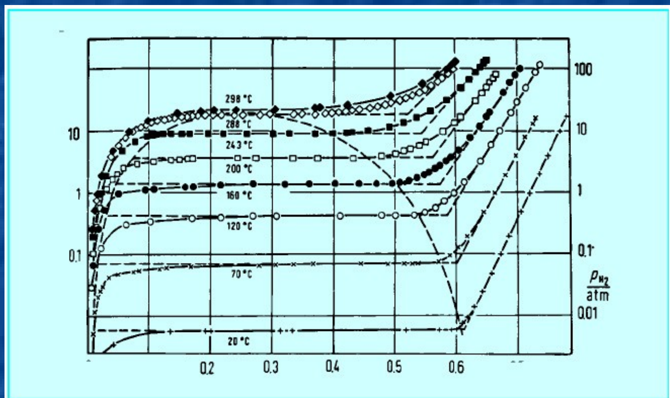
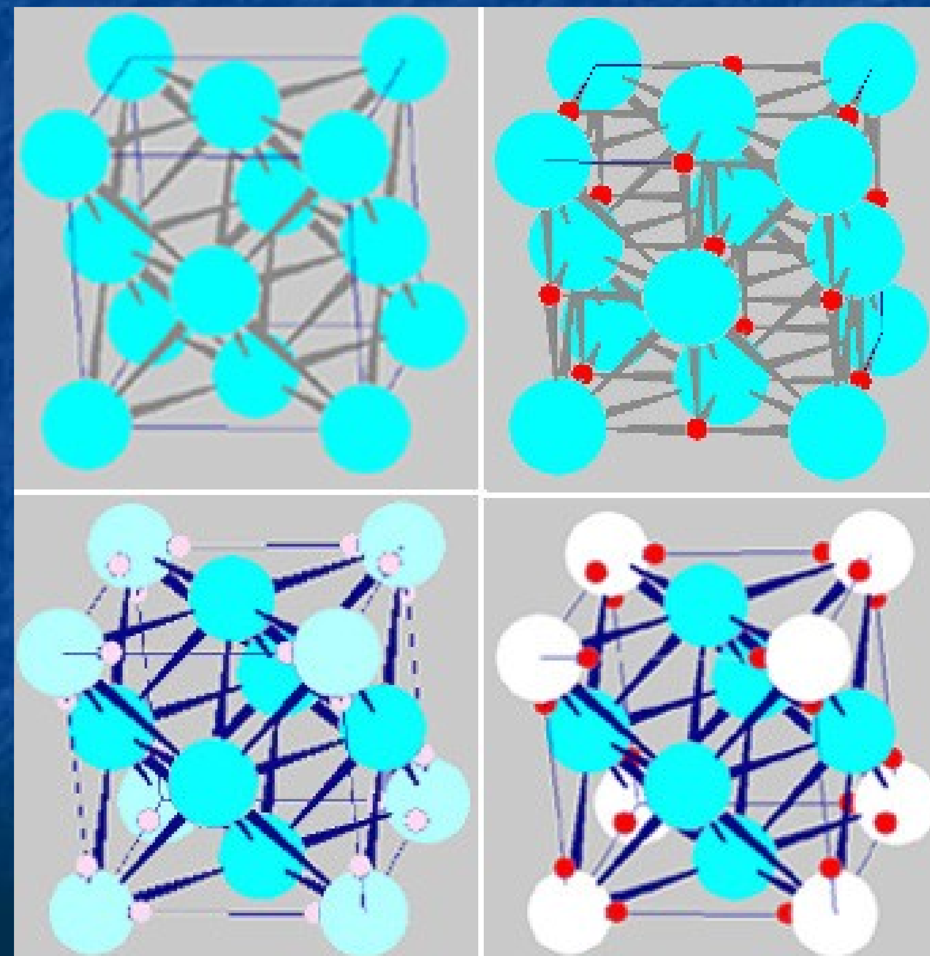


Diagramme d'état Composition-Pression à différentes températures du système palladium-hydrogène. La courbe de décomposition spinodale est clairement préfigurée par l'ensemble des isothermes.

Transformations de phases avec compétition des forces de liaison métal-métal, métal-hydrogène et métal-lacune.

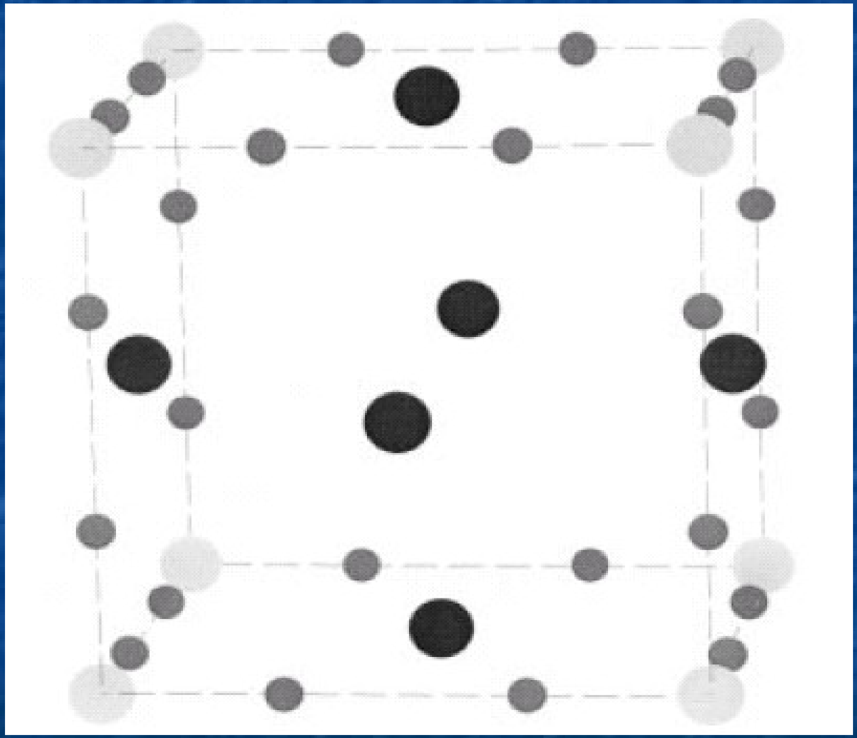
Diffusion métal x 10^3 à 10^5



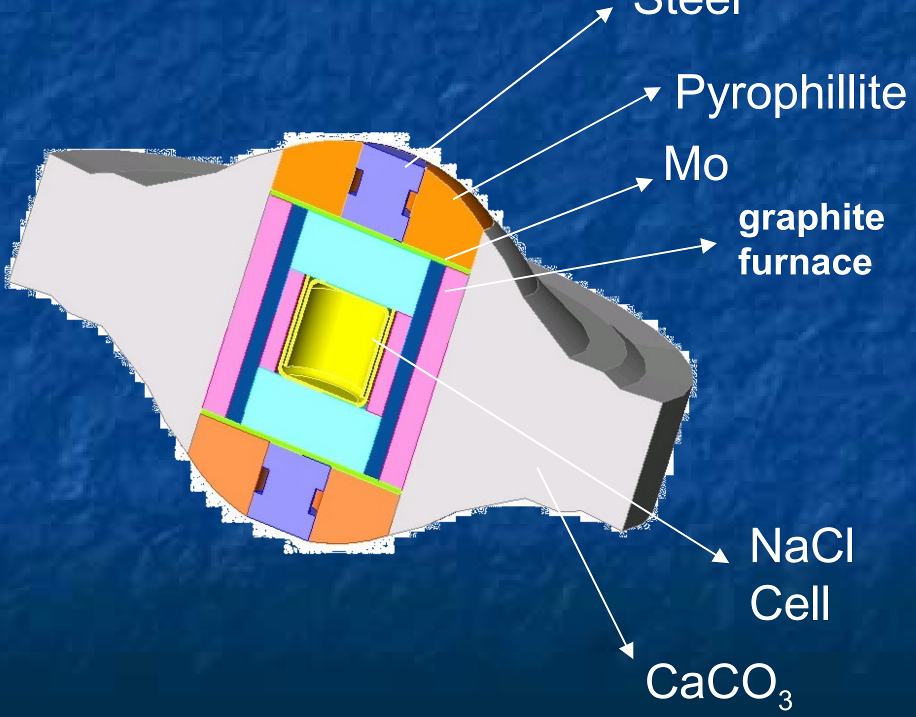
Hydrogen-induced vacancy structures in metals

- High pressure hydrogenation activates metal atoms diffusion

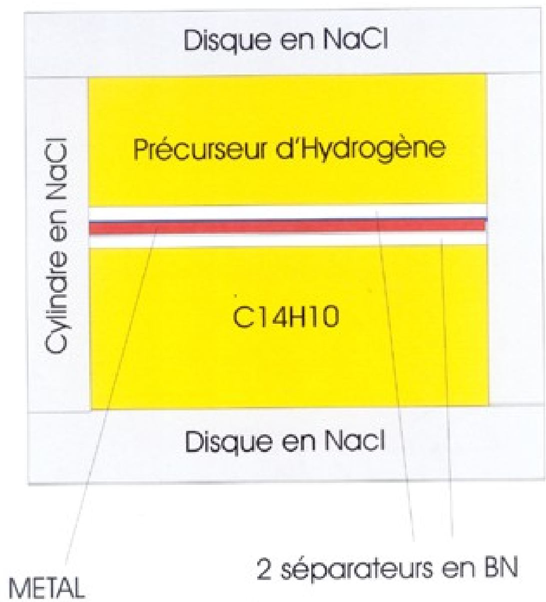
- Defect-hydride structures may be then stabilized



High Pressure hydrogenation



NANO-STRUCTURES METALLIQUES SOUS HAUTE PRESSION D'HYDROGENE ET A HAUTE TEMPERATURE



DIMENSIONS :

H : 7 mm; ϕ : 7 mm
épaisseur des parois de NaCl : 1 mm
épaisseur disque de métal : 0.1-0.2 mm
épaisseur disque BN : 0.1 0.2 mm

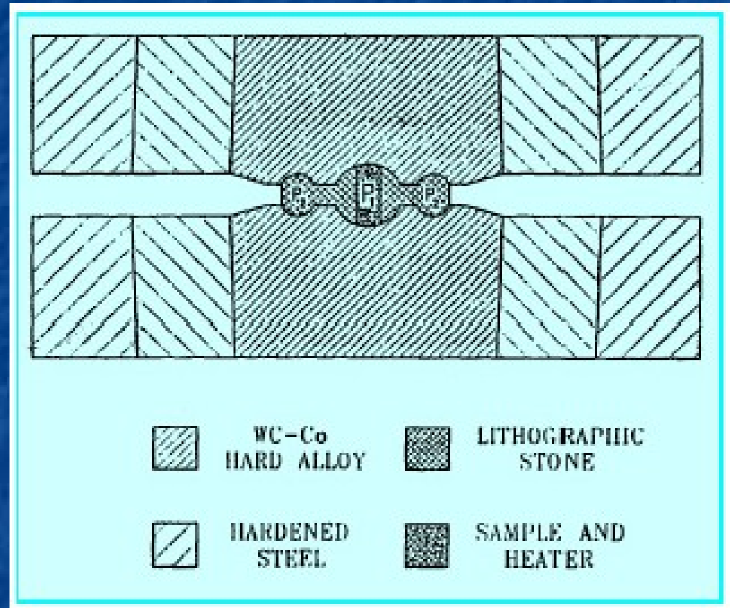
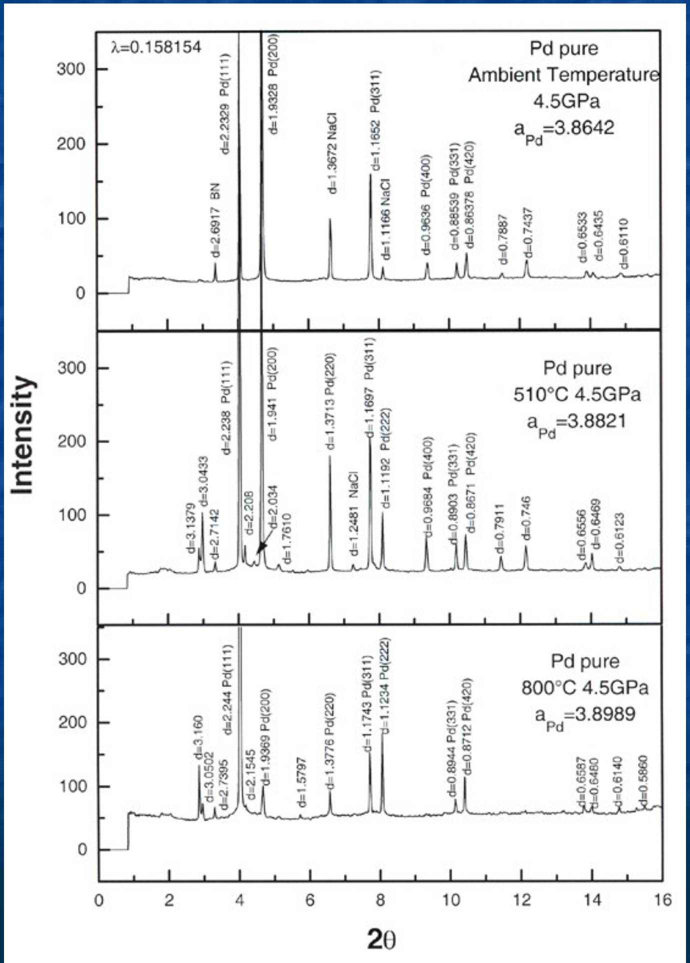
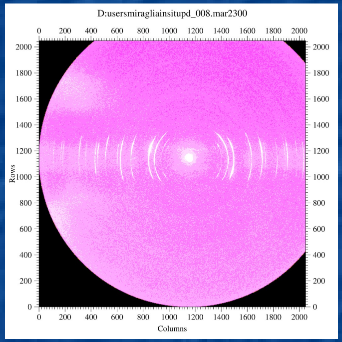


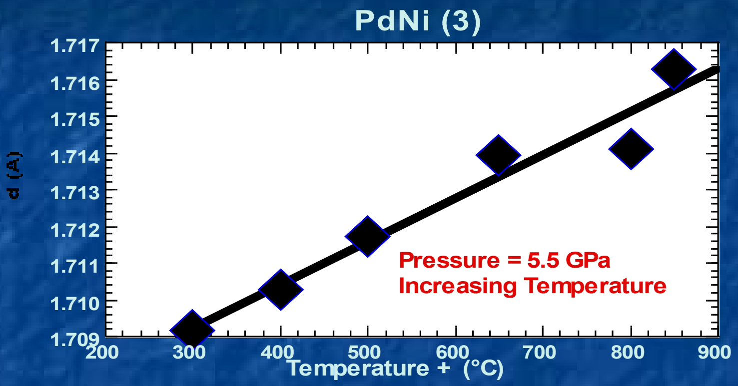
Schéma de l'enclume de type CONAC illustrant l'environnement et la position de la cellule.

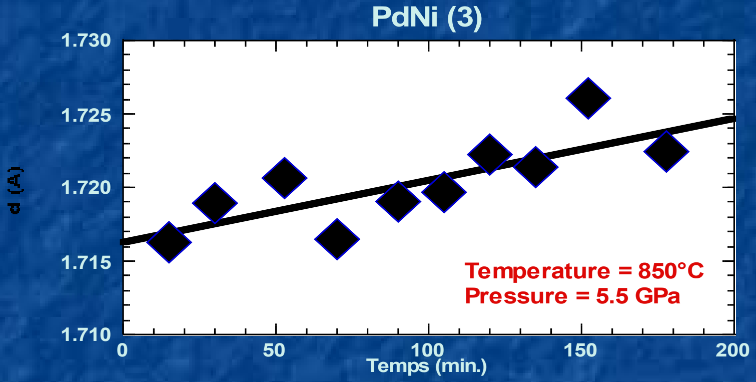
L'échantillon métallique est mis à réagir sous pression P > 3 GPa et en température T > 350°C (décomposition de $C_{14}H_{10}$)

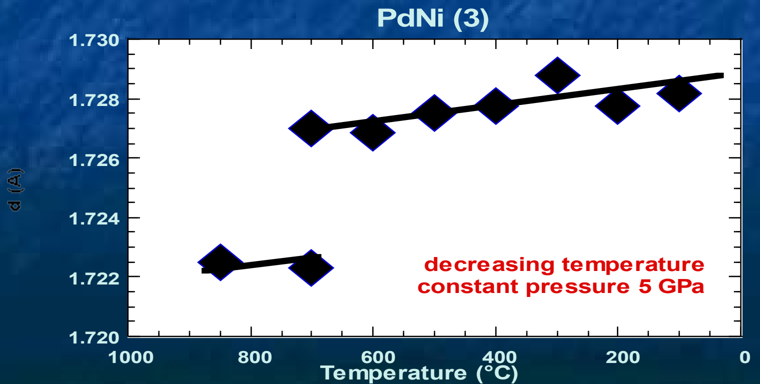
Synchrotron XRD studies



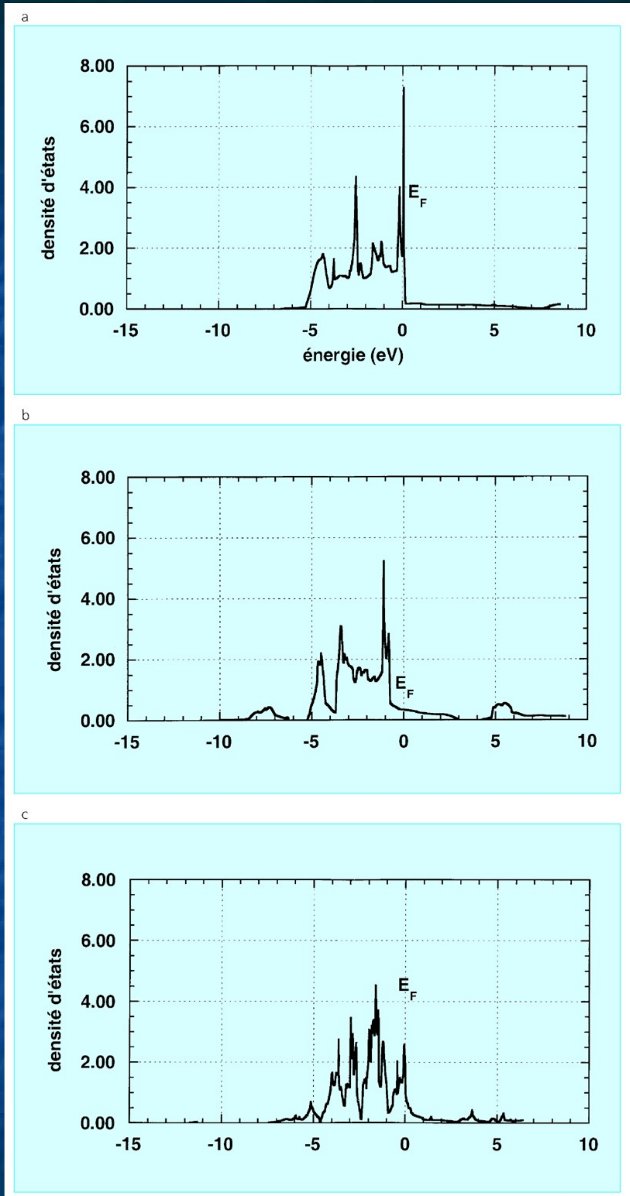




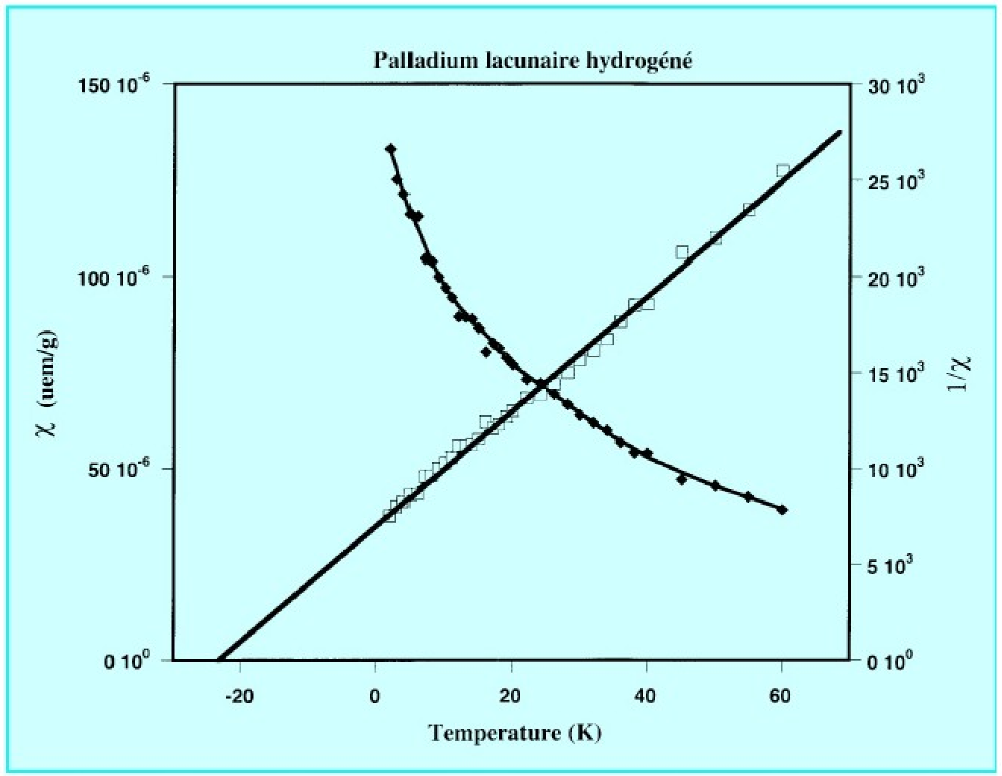




Physical properties

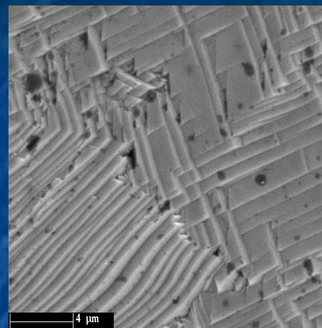


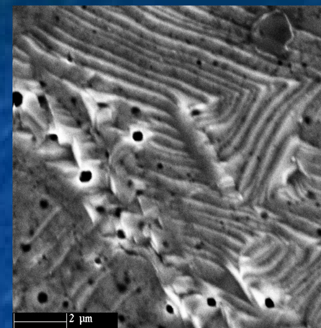
Densité d'états totale sur l'atome de palladium, calculée avec le code FLAPW.
a. pour le palladium métal (en bas),
b. le palladium hydruré « classique » $Pd_{Hx<1}$, (au milieu),
c. le palladium lacunaire hydruré (Pd_3(□-H_x)), (en haut).

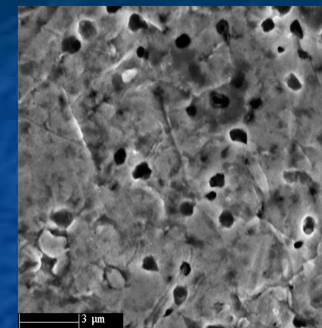


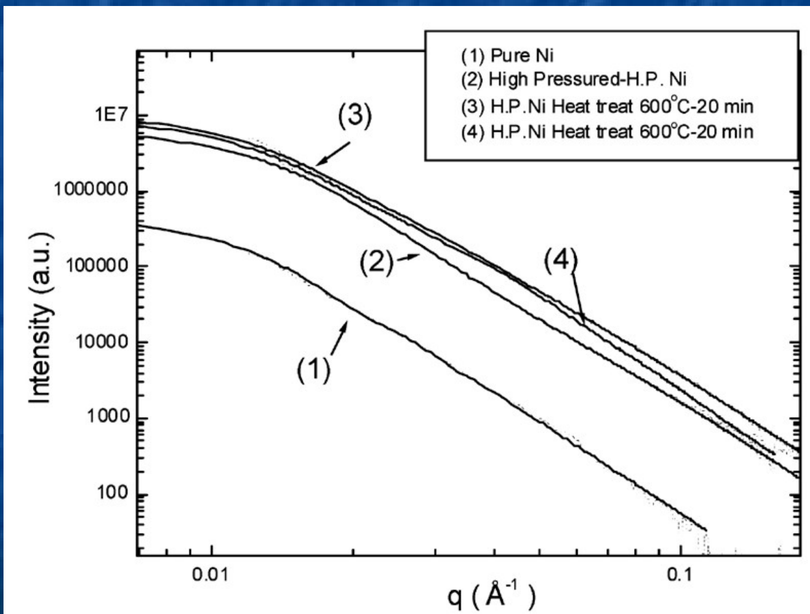
Susceptibilité magnétique et susceptibilité inverse du palladium lacunaire hydruré (Pd_3(□-H_x)).

Nano-pores in metals

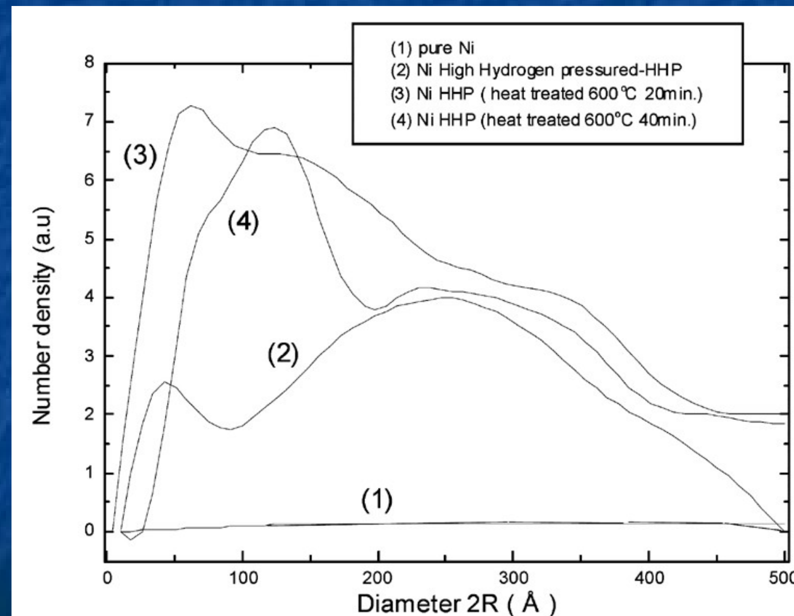








SAXS curves obtained for Ni submitted to a HHP of 3.5 GPa at 800 °C for 5 h, and subsequently heat treated at 600 °C for 20 and 40 min.



Size distribution of nanopores in Ni submitted to a HHP of 3.5 GPa at 800 °C for 5 h, and subsequently heat treated at 600 °C for 20 and 40 min.

Hydrogen-induced vacancy structures in metals

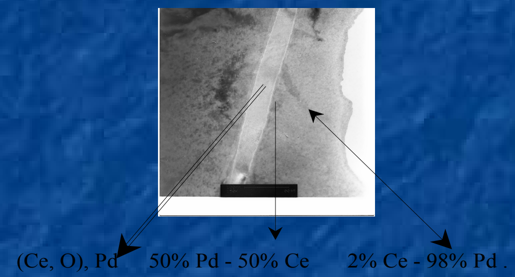
Vacancy coalescence in the dislocation-rich region (pore size = 50 nm)

- **Subsequent heat treatment gives way to vacancy coalescence resulting in nanoporous materials**
- **This technique of generating vacancies in a hydride phase provides a method to introduce vacancies in metals from which novel properties can be expected**

Oxide nanoparticles in a metal matrix

- **Controlled oxidization + subsequent high pressure hydrogenation leads to :**

$(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$

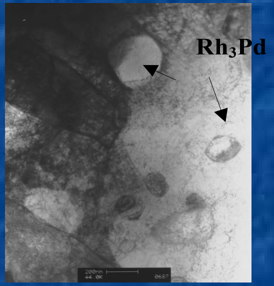


- **precipitation of oxide nanoparticles in the metal matrix (e.g. Pd-based)**

Oxide nanoparticles in a metal matrix

- **high pressure hydrogenation leads to hydrogen-induced phase separation**

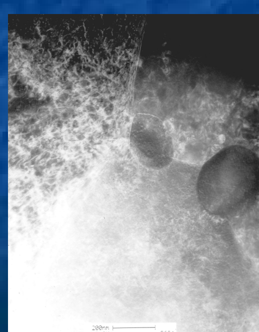
$(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$



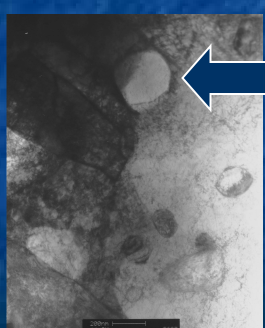
- **Active catalytic precipitates coherently distributed can be thus synthesized**

Investigation of two systems $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$, $Pd_{0.97}Al_{0.03}$, & $(Pd_{0.9}Pt_{0.1})_{0.97}Al_{0.03}$)

Prospective materials for catalysis



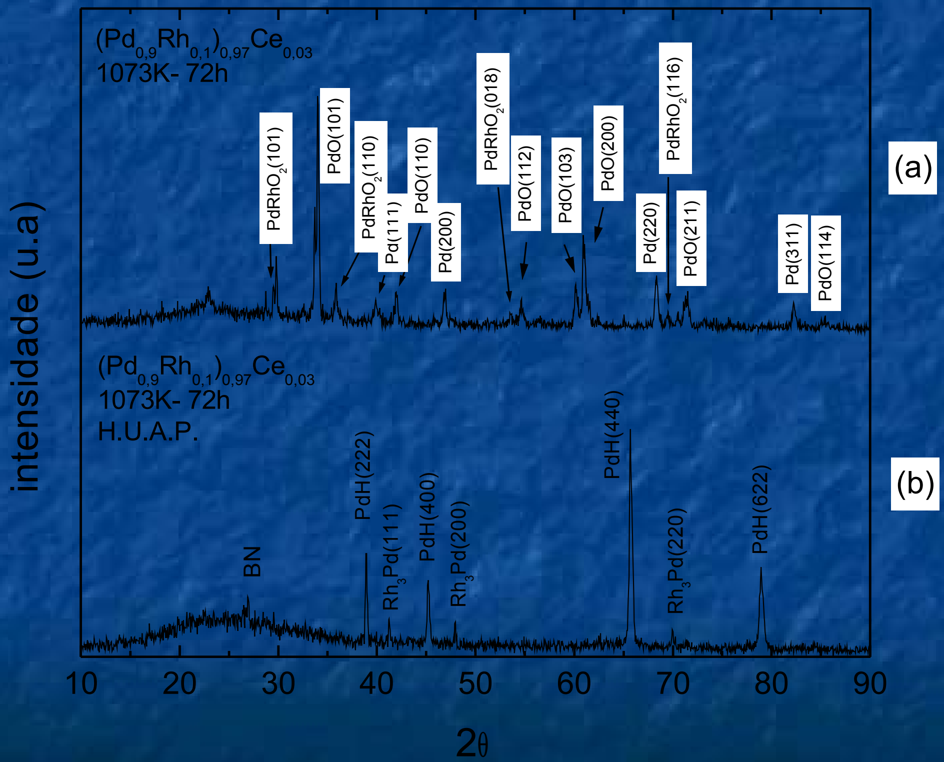
CeO_2

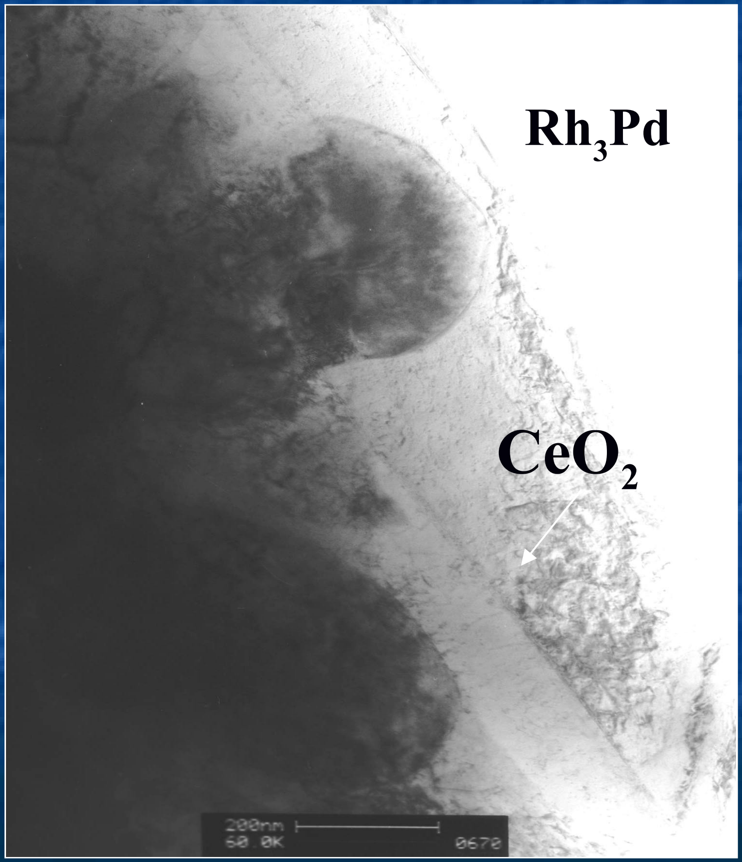


Rh_3Pd

$(Pd_{0,9}Rh_{0,1})_{0,97}Ce_{0,03}$ H.P.Hydrogenated
New Rh-rich phase

3,5 GPa – 5h – 800°C

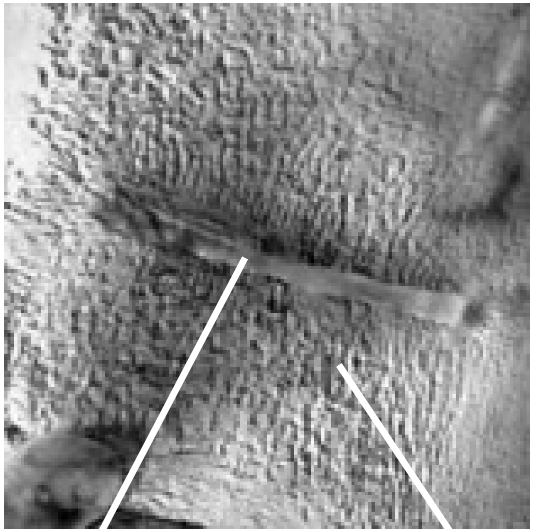




Azambuja V. et al.,Journal of Alloys and Compounds, Volumes 356-357, 11 August 2003

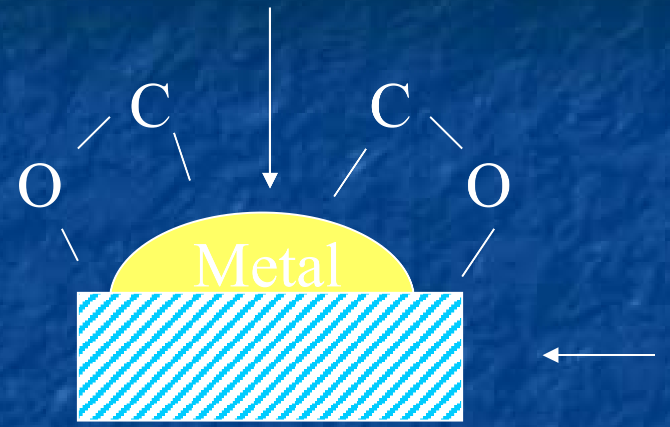
oxidization of PdCe

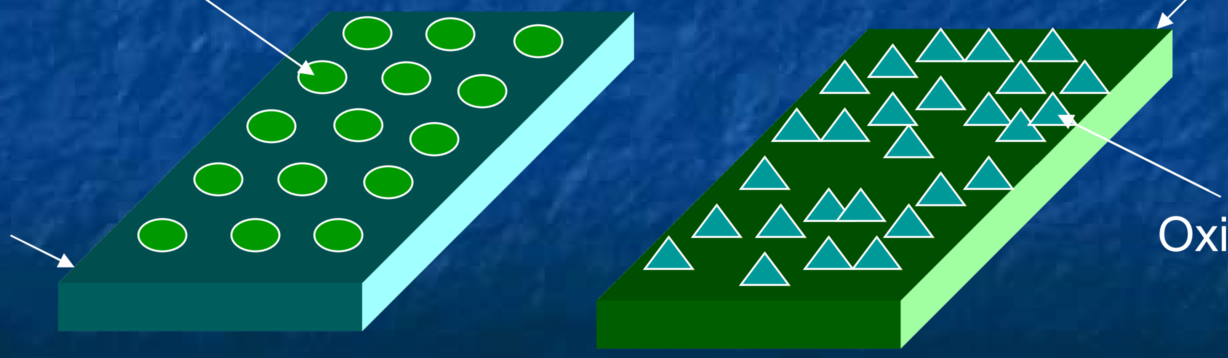
CeO2 intergrowth along [110] $_{Pd}$



Pd & Ce are substituted (antiphase)

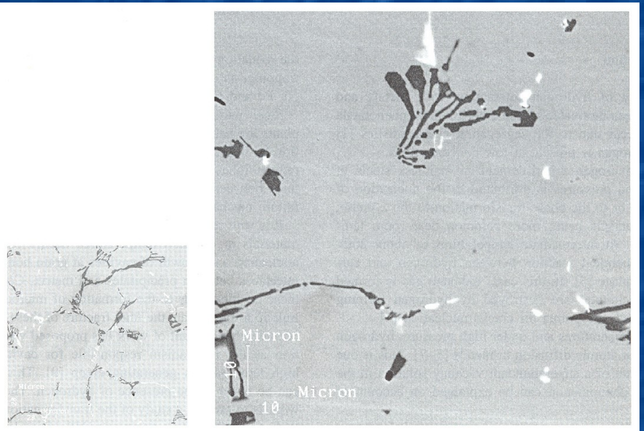
Metal-Oxide Composite



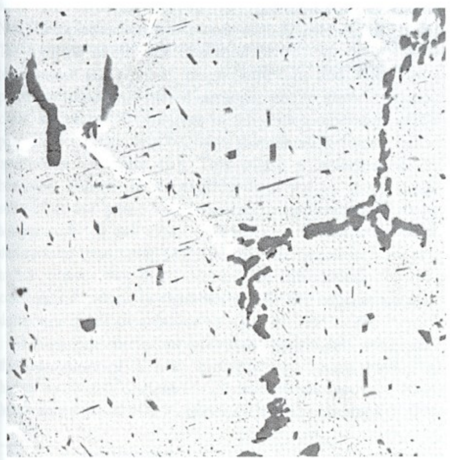


Special steels : enhanced metal fatigue under HP

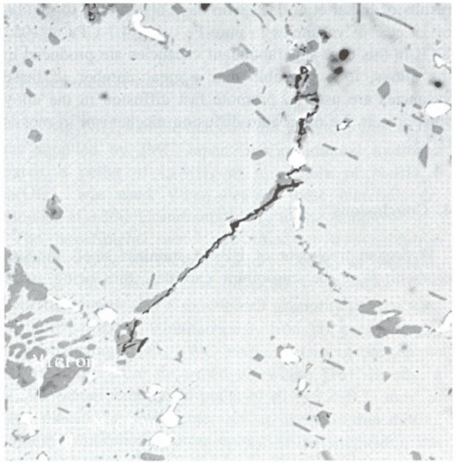
Aciers spéciaux pour forages pétroliers off-shore à grande profondeur
C : 0,41 - Cr : 25,5 - Ni : 34,9 - Mn : 1,03
Si : 1,91 - Nb : 0,78 - Ti : 0,04 - Fe : balance



Typical micrograph of the HP 45 stainless steel with Nb and Ti additions in the as-cast condition.



Microstructure of the HP 45 stainless steel after treatment with a low hydrogen pressure of 0.1 Pa for 100 h at 1200 K.



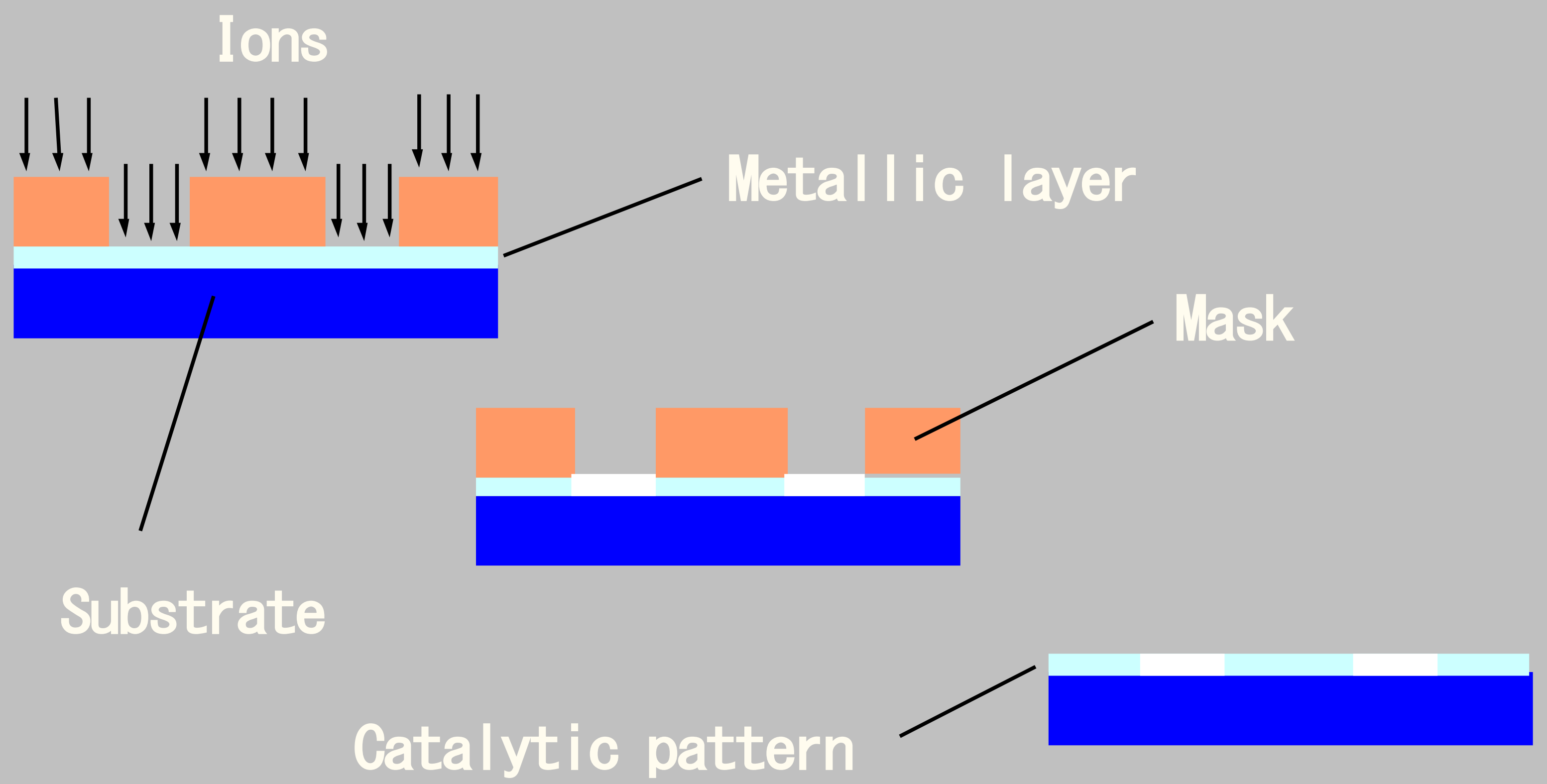
. Microstructure of the HP 45 stainless steel after treatment with a high-hydrogen pressure of 5 GPa for 1 h at 873 K.

Traitements de 100 à 1000 heures à environ 1200 K sous 0,1 Pa H_2 pour simuler le vieillisement des aciers ➡ La précipitation des mêmes matériaux de vieillissement aux joints de grains(ex : $(Nb,Ti)_{23}C_6$ = phase fragile) est réalisée en 1h sous 5 GPa et à moins de 900 K.

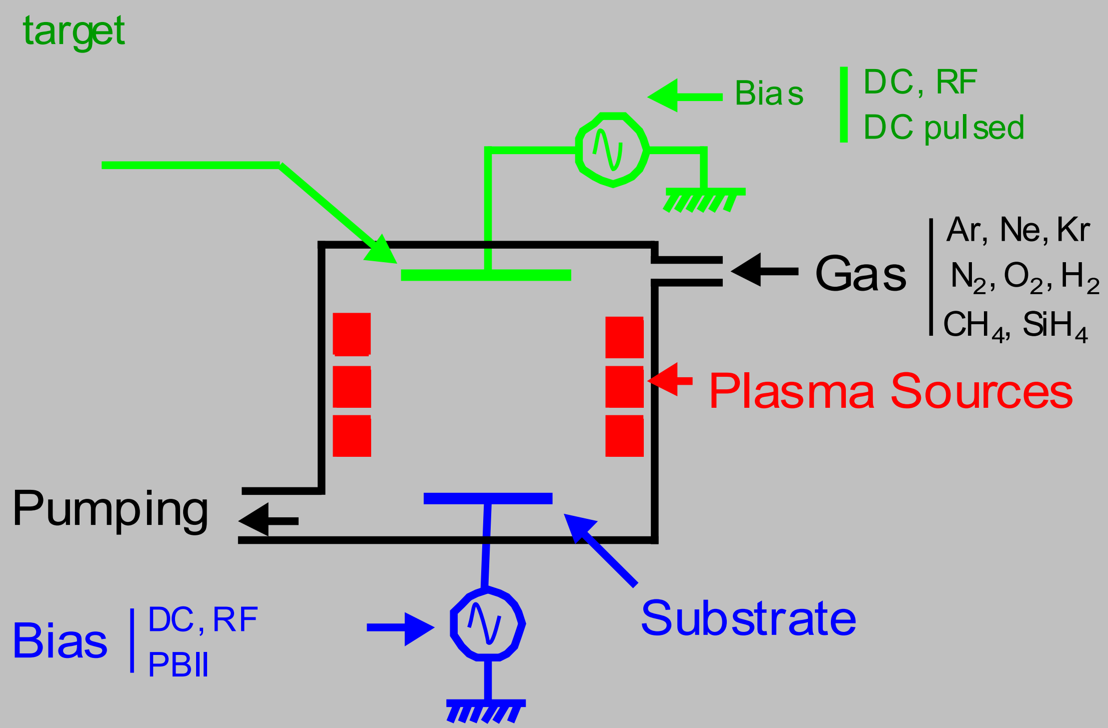
Plasma-based ion implantation (PBII) : a valuable technology for the elaboration of nanostructured thin films

- PBII used to tailor the surface and physical properties of nanoporous materials.
- Elaboration of nanostructures by implantation through a mask.
- Catalytic pattern obtained by implantation of catalytic species.
- Catalysts with active sites designed on the nanoscale can be obtained

tailoring catalytic patterns



PBII Reactor



Nanoporous alumina membranes

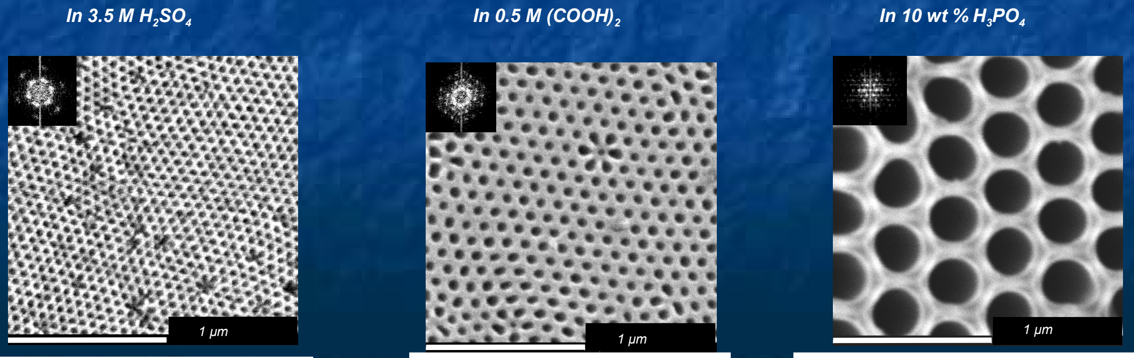
Ordered channels networks in alumina, resulting nanoporous membranes may be used as templates .

Masking with alumina membranes allows transfer of the hole pattern .

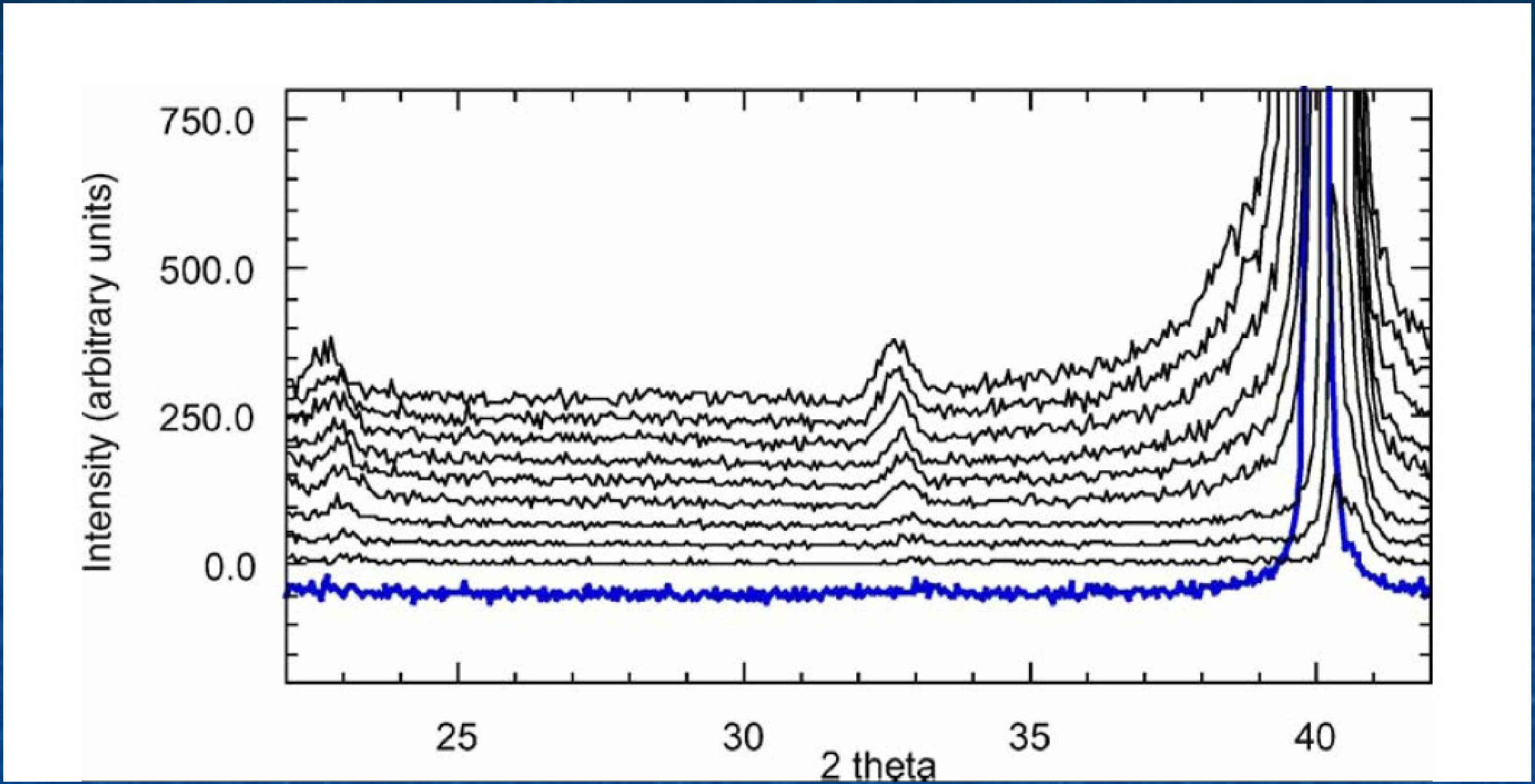
Porous structures (functionalized for catalysis) can be produced.

Resulting nanopore arrays are extremely well ordered and monodisperse.

These patterns can be used as templates or reference materials in the field of structural characterisation of porous media (SAXS, SANS).



Hydrogenation by means of PBII



- PBBI induces reordering of the f.c.c. lattice