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Retention and release (migration) behaviors of hydrogen in fusion reactor materials studied by tritium tracer techniques

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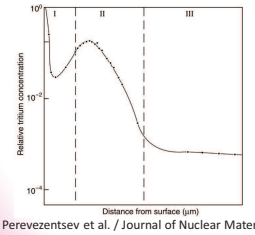
Summary of my talk

- Without knowing depth profiles of hydrogen in a solid and their sequential changes with time, analysis of hydrogen behavior by desorption and/or permeation to determine various parameters of diffusion, trapping and solution in the solid could result in wrong answers.
- The depth profile of hydrogen in a solid consists of at least four components, surface adsorbate, localized (trapped) one in near surface region, dissolved and trapped ones in bulk.
- Their relative amounts are quite dependent on hydrogen loading conditions and hydrogen solubility or a heat of solution (Exothermic or Endothermic)

Depth profile of hydrogen isotope (Past studies)

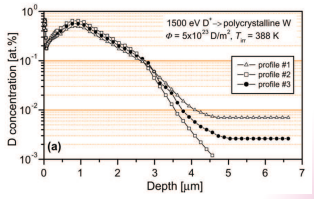
- ✓ Depth profiles of H(D,T) loaded in metals have been extensively studied. However, most of them are limited to near surface region. Even in such limited region, the profiles often consist of several components.
- ✓ Moreover, they are not well correlated with a dissolved component and/or trapped one in deep inside.
  → Need profiles in a deeper region of bulk !

Gas absorption (SS304)



A.N. Perevezentsev et al. / Journal of Nuclear Materials 372 (2008) 263–276

Ion implantation (Pure W)



V.Kh. Alimov et al. / Nucl. Instr. and Meth. in Phys. Res. B 234 (2005) 169–175

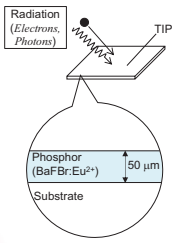
Depth profiling of tritium

Tritium Imaging Plate Technique (TIPT) is useful !

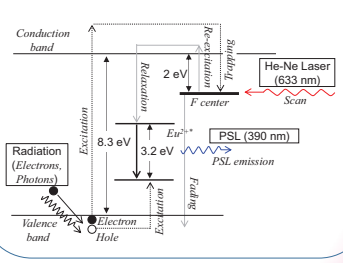
- ✓ Visualization of depth profiles of T (hydrogen) from several tens μm to cm order
- ✓ More than 5 digits in detection of T amounts

Mechanism of photo-stimulated luminescence process in BaFBr:Eu^{2+} phosphor layered in TIP (After Iwabuchi *et al.*)

- ✓ 2-dimensional detector of deposited energy by radiation of electrons and photons



Energy levels in BaFBr:Eu^{2+}



- ✓ Unit of T intensity (radioactivity) is (PSL mm^{-2} s^{-1})

Depth profiling of tritium

Tritium Imaging Plate Technique (TIPT) is useful !

- ✓ Visualization of depth profiles of T (hydrogen) from several tens μm to cm order
- ✓ More than 5 digits in detection of T amounts

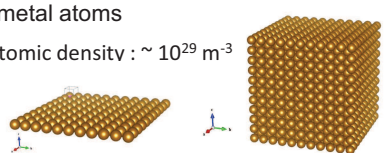
Investigated are

- Penetration (diffusion and trapping) behaviors of hydrogen loaded by gas absorption and plasma injection into the F82H steel and pure tungsten (W)
- Release behavior of loaded hydrogen by observing sequential changes of the depth profiles with time and temperature

Comparison of density of host (metal) atoms and concentration of dissolved H in the host

Density of host metal atoms

- ✓ Volumetric atomic density : ~ 10^{29} m^{-3}



- ✓ Atomic density of metals in one layer (~ 0.3 nm) : ~ 10^{19} m^{-2}/layer

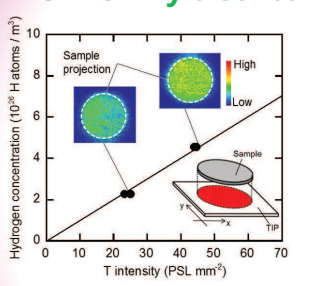
H concentration in metals

Hydrogen loading by gas absorption under 0.1 atm and at 573 K

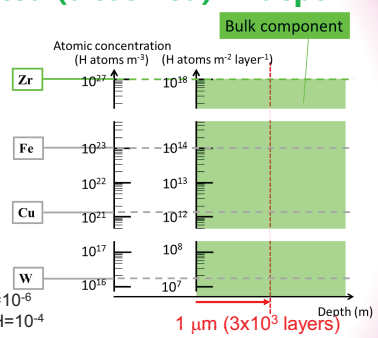
Exothermic hydrogen occluder,
Zirconium (Zr): 10^{27} m^{-3} ≈ 10^{18} m^{-2}(layer^{-1}) (up to 100%)
Endothermic hydrogen occluder,
Tungsten (W) : 10^{16} m^{-3} ≈ 10^{7} m^{-2}(layer^{-1}) (ppm or below)

T loaded by gas absorption in Zr

Uniformly distributed (dissolved) in depth



10 (PSL mm^{-2}) ≈ 0.1 at-%(Zr) @ 1h, T/H=10^{-6}
10 at-ppm(Zr) @ 1h, T/H=10^{-4}

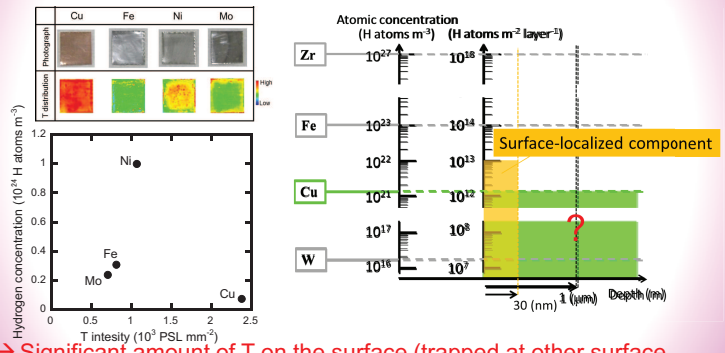


- ✓ Escaping depth of T β electrons in metals is ~ 1 μm

Tritium (Hydrogen) concentration in bulk is closely related to T intensity measured by TIP → Quantification of T from a master curve

T loaded by gas absorption
Tritium profiles on surfaces of Cu, Ni, Fe, Mo

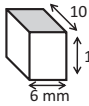
✓ No correlation between T at surface and T dissolved in bulk



→ Significant amount of T on the surface (trapped at other surface adsorbates (Impurities layers) and/or mechanically formed defects ?)

Tritium loading by Plasma
@ Kyushu University

- Sample: Reduced activation ferritic/martensitic steel (F82H)



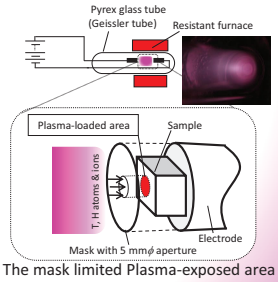
C	Cr	W	V	S	Fe
0.09	7.84	1.98	0. 19	0.001	Bal.

(wt%)

- T loading condition

T concentration: T/H=1.3 x 10^{-4}
Discharged Voltage: 400 V
Ion current: 0.13 A m^{-2}
Loading temp.: 298 – 673 K
Duration: 1 - 2 h

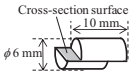
* Cooling by quenching the glass tube



✓ The mask limited Plasma-exposed area

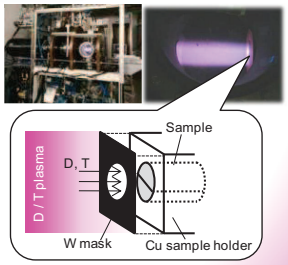
Tritium loading by plasma
@Idaho National Laboratory, US

- Sample: Pure W (Purity: 99.99 %, ALMT, JPN)



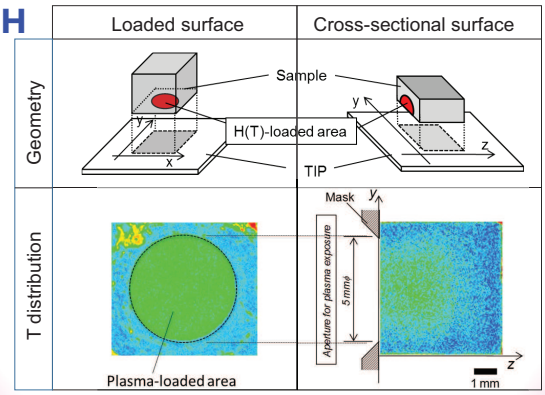
- TPE condition

T concentration: 0.1 – 0.2 %
Flux: 5 x 10^{21} m^{-2} s^{-1}
Fluence: 3.5 x 10^{25} m^{-2}
Bias Voltage: -100 V
Duration: 2h
Loading temp.: 393 – 673 K
Duration: 2 h → Cooling in vacuum



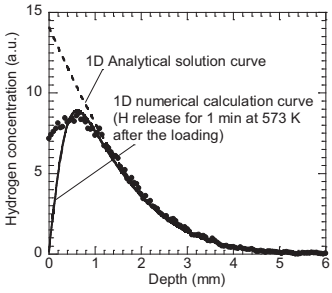
Observation of T distribution on the cross-section surface

F82H



Depth profile of plasma-loaded T

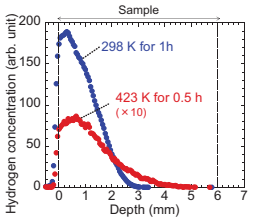
F82H

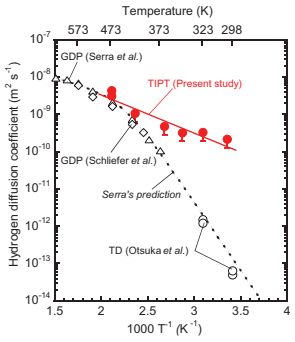


✓ Deeper penetration up to 4 mm
✓ Release from the loaded surface after the loading
→ Diffusion behavior !

Diffusion coefficient determined from the dissolved component in F82H

F82H

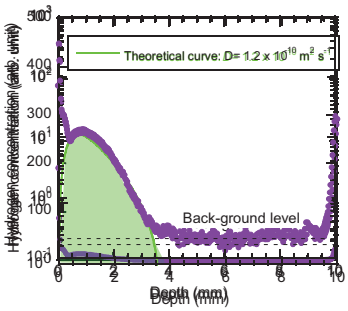




✓ Good agreement with high temperature data above 473 K
→ Reliable data as interstitial hydrogen diffusion coefficients
* Isotope effects are negligible within experimental errors

Depth profile of plasma-loaded T in pure W (573 K)

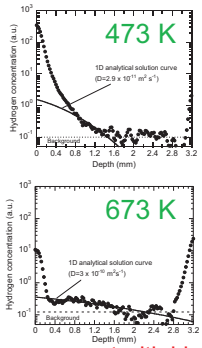
W

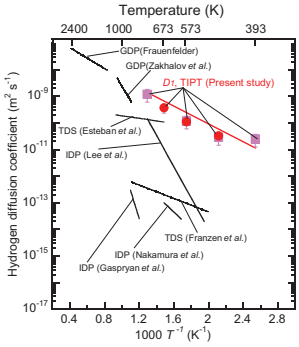


✓ Less penetration up to 500 μm in Linear scale
✓ Deeper penetration more than 4mm in depth appears in logarithmic scale → Diffusion behavior !

Diffusion coefficient determined from the dissolved component in W

W

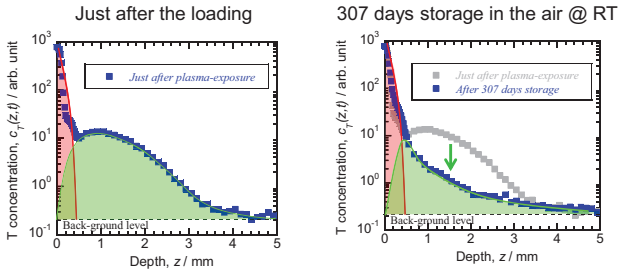




✓ Good agreement with high temperature data (Frauenfelder) above 1173 K →Reliable data as interstitial hydrogen diffusion coefficients
* Isotope effects are negligible within experimental errors

Release of dissolved (Diffusion and Trap) components in deeper region during storage in air at RT

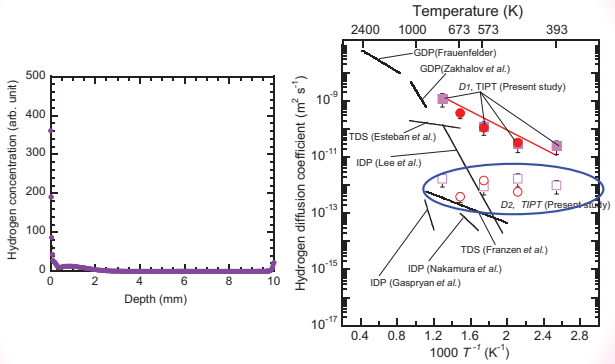
W



✓ The surface-localized component remained longer than the bulk (Diffusion and Trapping) components → Strong hydrogen trapping at impurities or defects newly formed by plasma-loading

Depth profile of surface-localized component

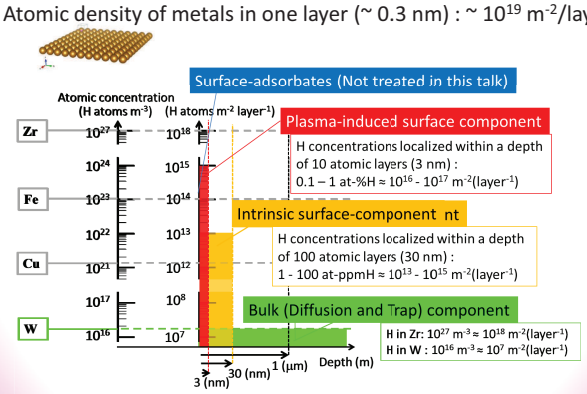
W



✓ Most of previous reported diffusion coefficients are very likely determined from hydrogen trapped in near surface region

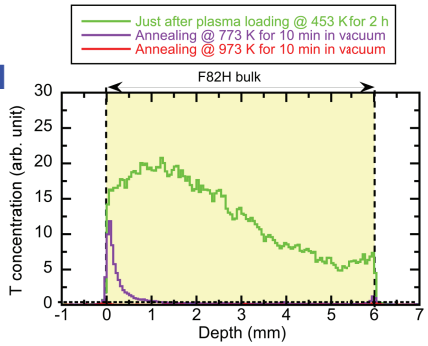
Comparison of absolute amounts: Four components in depth profile of T

✓ Atomic density of metals in one layer (~ 0.3 nm) : ~ 10^{19} m^{-2}/layer



Changes of depth profile of T by annealing at constant temperature

F82H

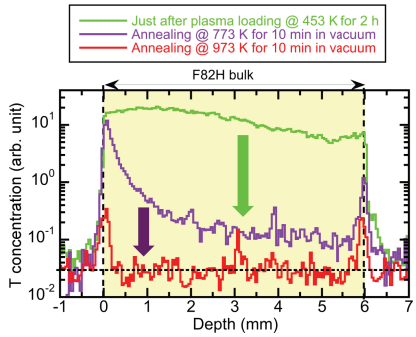


✓ Dissolved component was mostly released by diffusion

✓ Surface trapping decreased; still some remained.

Detailed depth profiles after thermal annealing

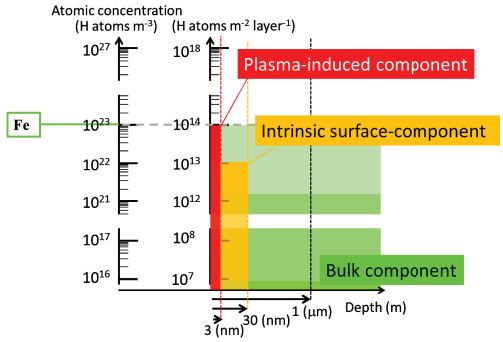
F82H



✓ T trapped at front-surface (plasma-loaded side) could be removed by high temperature annealing, but still some remained

* T amounts trapped at the both surfaces become comparable

For analysis of hydrogen behavior by thermal desorption



✓ Knowing depth profiles of hydrogen in deeper region of bulk and their sequential changes with time is important!!

Conclusions

Exothermic H occluders

- Irrespective of H loading condition, H tends to be dissolved uniformly with its amount much larger than other components (surface adsorbate, trapped ones in near surface region and bulk)

Endothermic H occluders

- Relative amounts of four components are quite dependent on H loading conditions. In most cases, the concentration of surface trapped H surpasses that of dissolved one which is easily desorbed by diffusion because of rather large diffusion coefficients.
- Energetic H injection significantly enhances trapping in near surface regions. W is a typical example showing quite different trapping phenomena depending on the loading condition.

Summary for fusion application

■ **Surface- and near surface localized components**

◆ **H in surface adorbates (= top surface)**

- Any materials surfaces adsorb H atoms and its compounds like water and hydrocarbon molecules
- Easily replaced with loaded T by isotopic exchange reactions

◆ **H in intrinsically modified surface layers (≤ sub-surface layers – 100 layers)**

- Protective or passive oxide layers or coverage of some other precipitates (like carbides, sulfides, nitride and their mixtures) with thickness of a few tens nm.

◆ **H in defects/impurities induced by H loading (≤ 10 layers)**

- Key factors controlling tritium retention and release behaviors (3 or 4 orders of magnitude larger than diffusion component !)
- Effect of rapid isotopic exchange at sub-surface layers
- Quasi-independent retention and release (Remain longest indicating strong trapping near surface region)

■ **Bulk component**

◆ **H in far deeper region (>> 1mm in depth)**

- Not so large impact on tritium retention due to very low hydrogen solubility in pure W
- Penetration by simple lattice diffusion for cumulative retention in the bulk and permeation leakage to the surroundings

→ Our data (473 K - 673 K) + Frauenfelder data (>1173 K) are recommended.

Thank you for your attention !!