Ion irradiation effects of oxide scales on the corrosion rate of zirconium alloys

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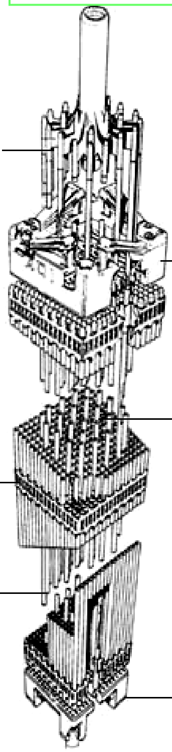
In the PWR core, the fuel pellets are stacked in zirconium based alloy claddings



Operating conditions :

- Temperature : 300 – 330 C
- Pressure : 155 bars
- Water chemistry : 0.7 – 2.2 ppm Li, 10 – 1200 ppm B
- pH : ~ 7.2
- Dissolved hydrogen : 25 – 50 cm^3/kg

Zirconium based alloys :

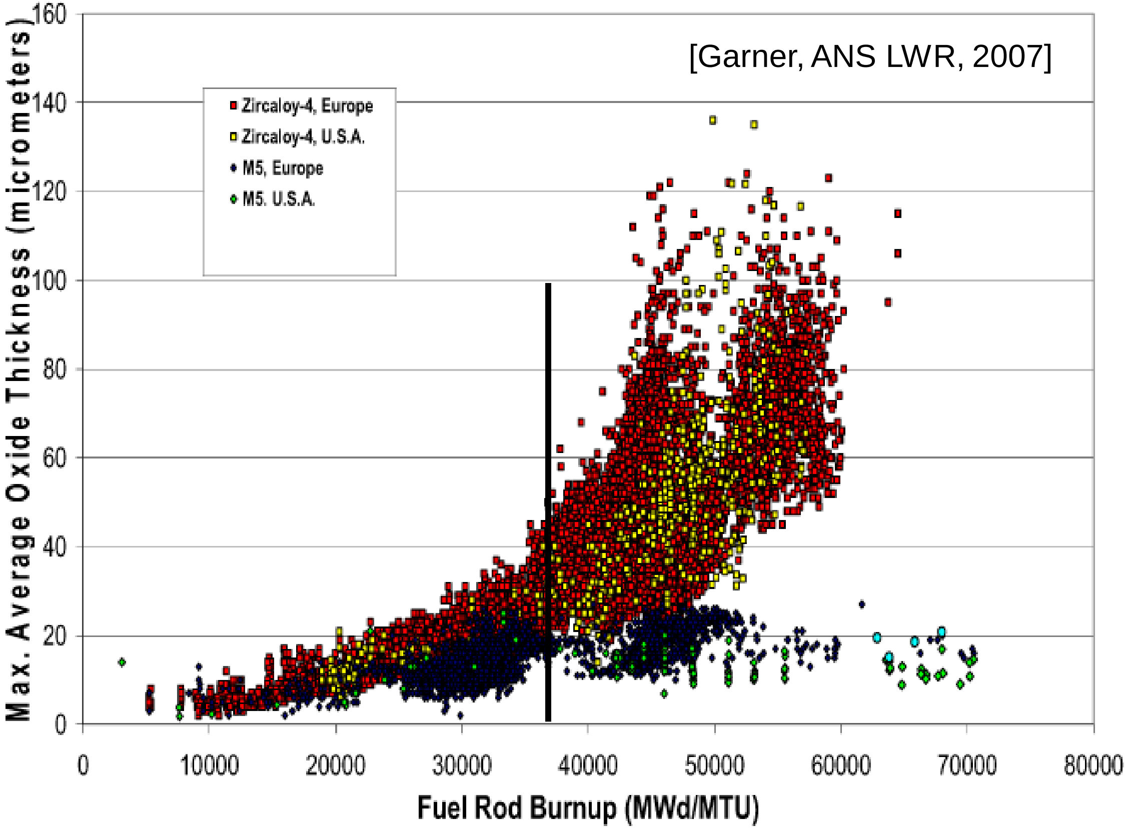
- Zircaloy-4 : Zr-1.3Sn-0.2Fe-0.1Cr-O
  - Sn, O : solid solution
  - Fe, Cr => $Zr(Fe_{1-x}, Cr_x)_2$ (Laves phases/SPP)
- M5® : Zr-1Nb

Researched properties :

- neutron transparency
- good mechanical properties
- satisfactory corrosion resistance

Comparison of M5® and Zircaloy-4 performance in PWR

$$Zr + 2\,H_20 \rightarrow ZrO_2 + 2\,H_2$$



Zircaloy-4 : « phase III » acceleration

M5 : no kinetic acceleration beyond 40GWd/tU

⇨ **External corrosion of Zy4 claddings : limiting factor of the lifetime**

⇨ **Working hypothesis : irradiation effect ?**

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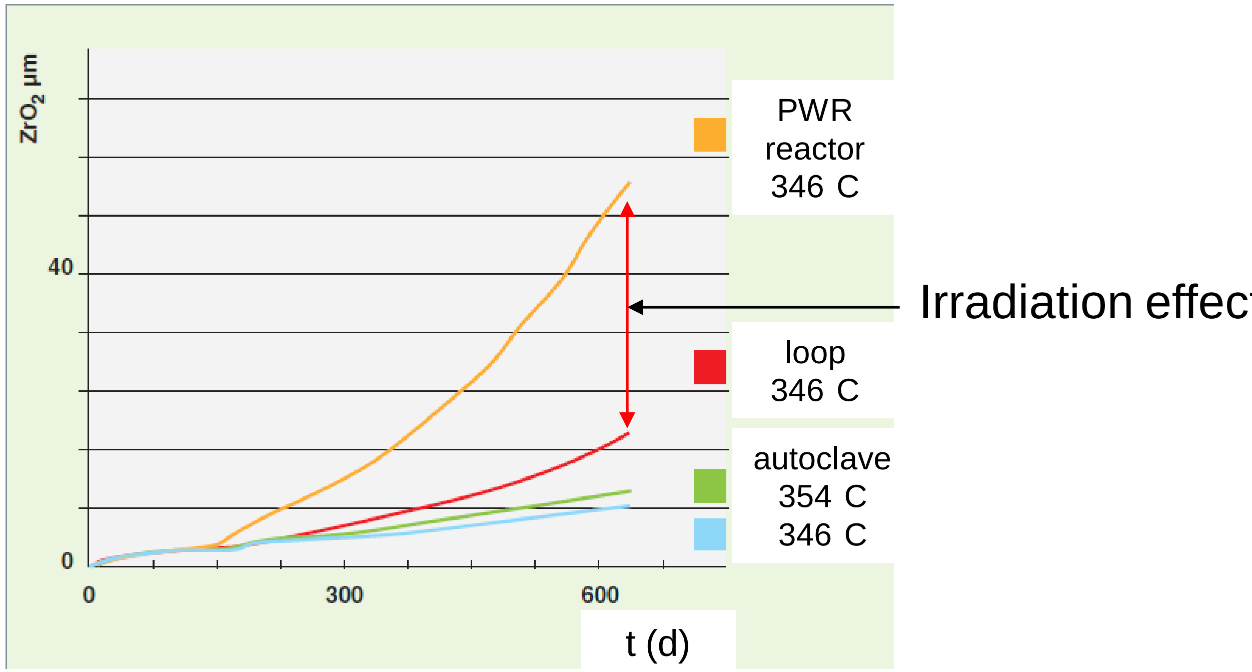
Corrosion kinetics in different operating conditions

Zircaloy-4



[CEA Saclay, Monographie DEN, 2008]

⇨ strong irradiation impact

⇨ **but on what ?**

- Metallic matrix
- Oxide
- radiolysis

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Irradiation impact on the microstructure of the claddings and corrosion kinetics

- **Effect on the metallurgical state of the alloy** :
  - Laves phases not stable under irradiation
  - amorphisation/ dissolution of the SPPs

- **Impact on the oxide microstructure and on the corrosion kinetics :**
  - defect formation : change of the diffusion properties, the electronic and thermal conduction…
  - phase transformation (monoclinic – quadratic zirconia) [Simeone,JNM 2002]

- **Influence on the chemical environment :**
  - radiolysis → radiolytic species formation
  - dissolution of zirconia

⇨ Role of these effects on the corrosion behavior

Effect of oxide irradiation on the corrosion

1. To better understand the corrosion mechanism :

⇨ Local irradiation of the metal/oxide interface with protons or helium ions

2. To quantify the defect concentration dependancy on the oxygen diffusion rate :

⇨ Uniform damage (not presented)

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Why irradiate the interface of the oxide scale **??**

Corrosion mechanism of Zy4 during the pre-transition stage :

- internal development of the oxide + n-type semi-conductor
- corrosion rate limited by vacancy diffusion in the oxide scale

$$V_{ox} \alpha J_V \alpha D_v(\Delta C_v/X) \sim D_v(C_{vi}/X) \quad \text{i.e. } C_{ve} << C_{vi}$$

Expected results :

⇒ *Zy4 : increase of corrosion rate after irradiation of the metal/oxide interface*

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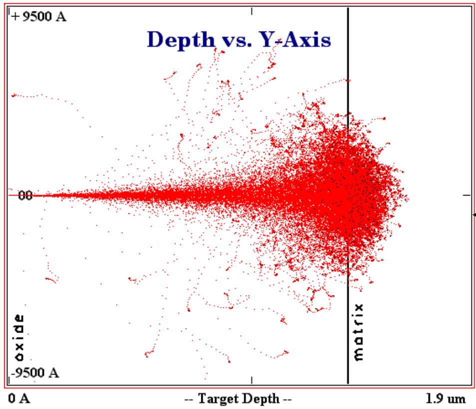
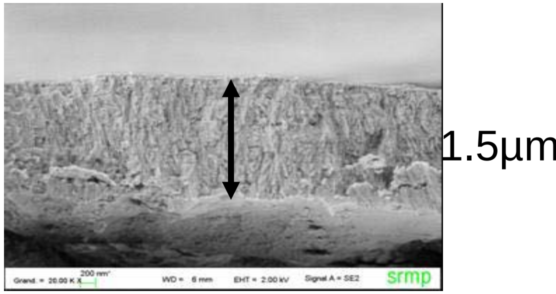


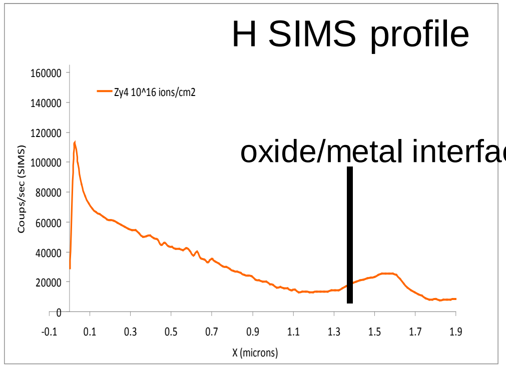
Experimental process : 5 steps

- Pre-oxidation of Zy4 polished sheets until a 1.5 µm oxide thickness in PWR conditions



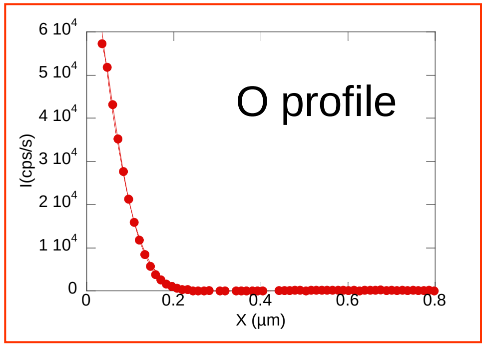
- Proton irradiation with ARAMIS facilities in ORSAY

- SIMS analyses of hydrogen implantation



- Re-oxidation in a $H_2{}^{18}O/D_2{}^{16}O$ (20/80%) mixing during 24 hours

- SIMS analyses of the oxygen and deuterium profiles



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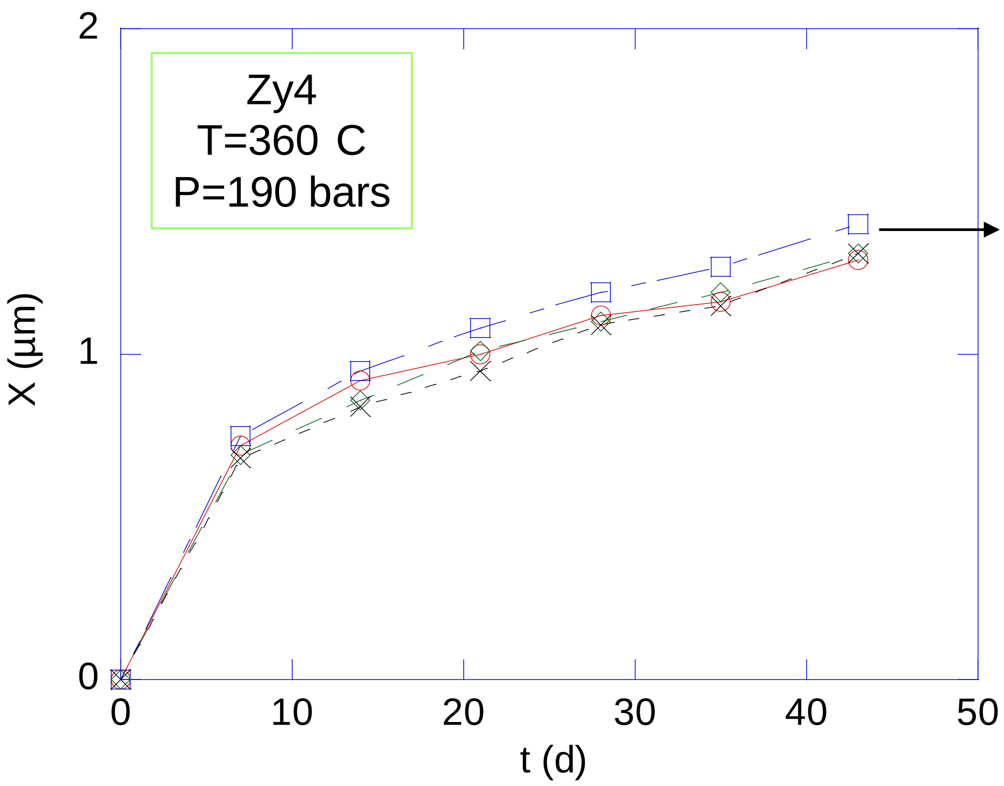
Step 1 : oxidation kinetics **before irradiation**



X_{Zy4}**=1.4 µm**

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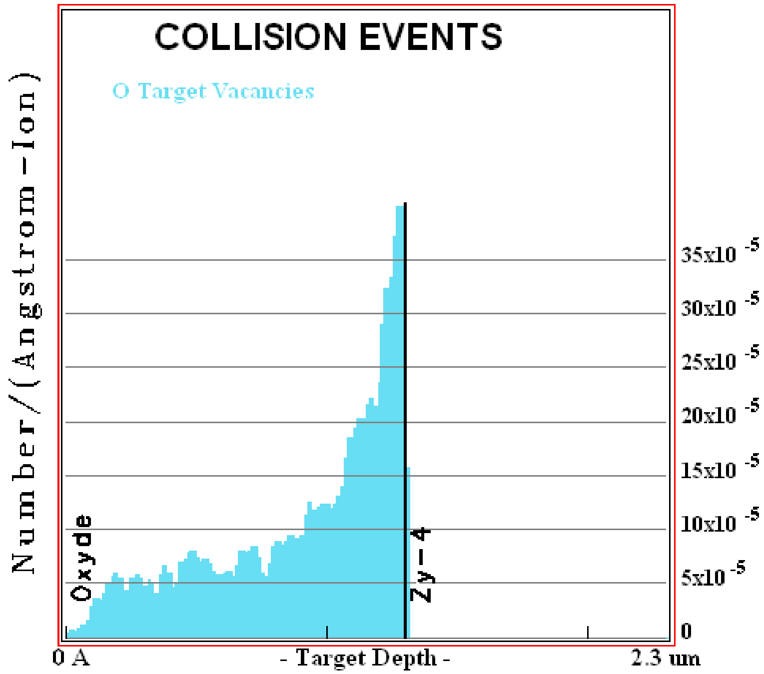
Step 2 : simulation of irradiation damage with SRIM

• chosen ion and incident energy : **H^+ 250keV**

• **production of defects at the metal/oxide interface**



⇨**highest concentration of defects localized near the metal/oxide interface**

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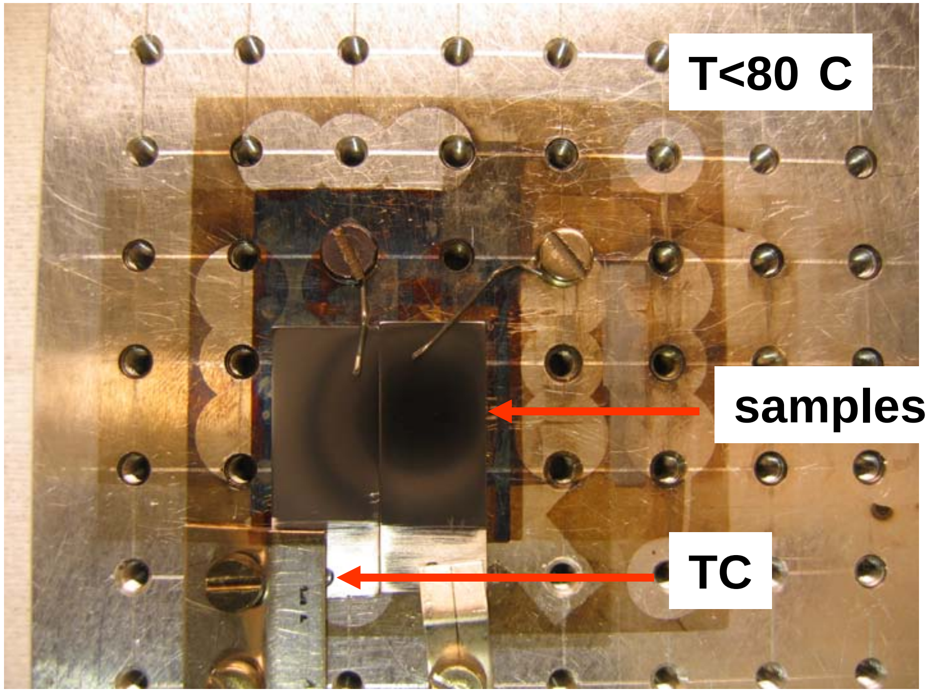
Step 2 : computation of irradiation damage with SRIM

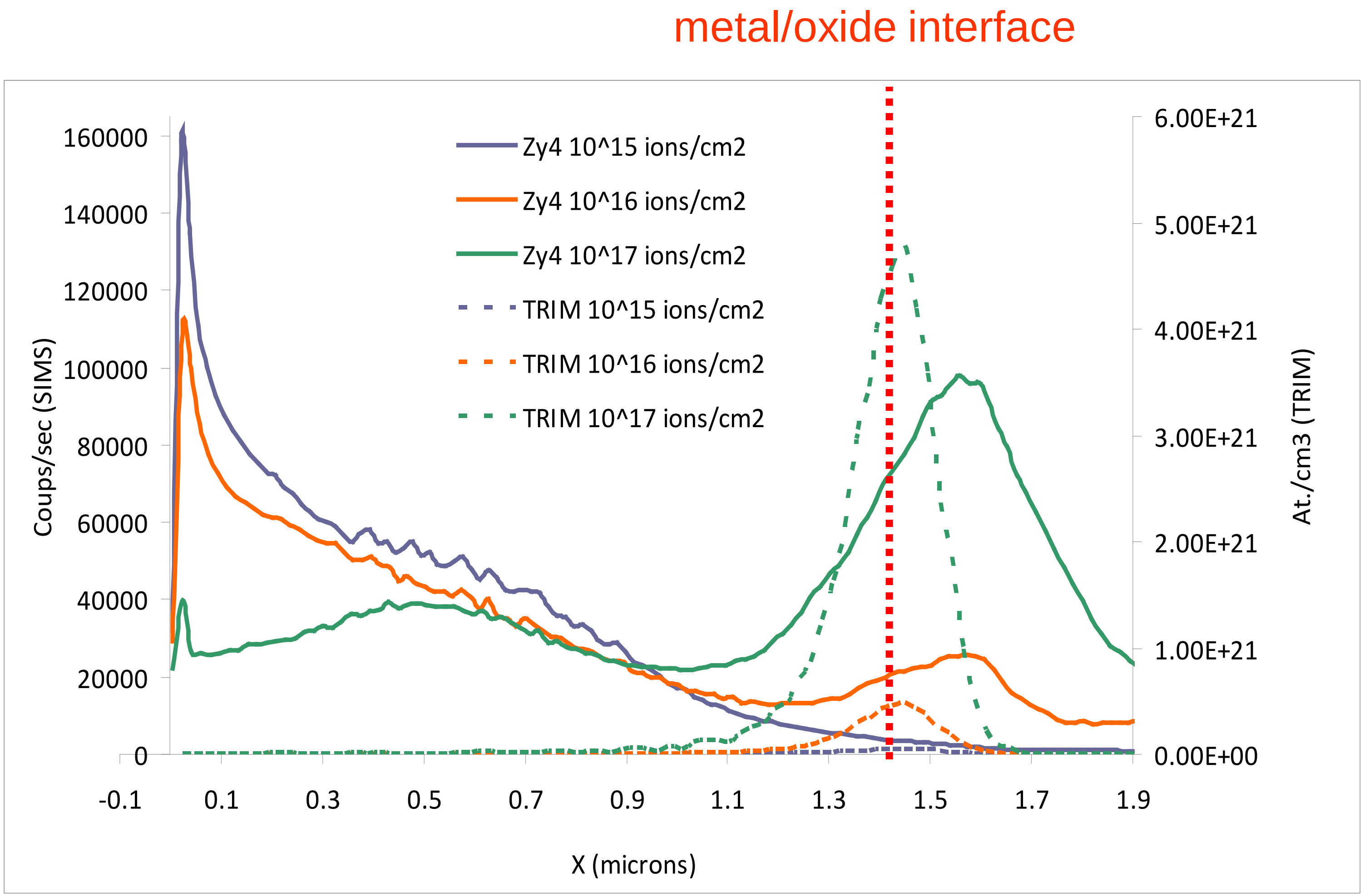
- Irradiations performed with ARAMIS facilities at the CSNSM Orsay
- Incident ions : $\mathbf{H_2^+}$ **500keV**

N° sample	**66a**	**67a**	**69a**
Fluence (ions/cm^2)	10^{15}	10^{16}	10^{17}
dpa	**2.10^{-3}**	**2.10^{-2}**	**2.10^{-1}**
% vacancies /O	0.07	0.7	7



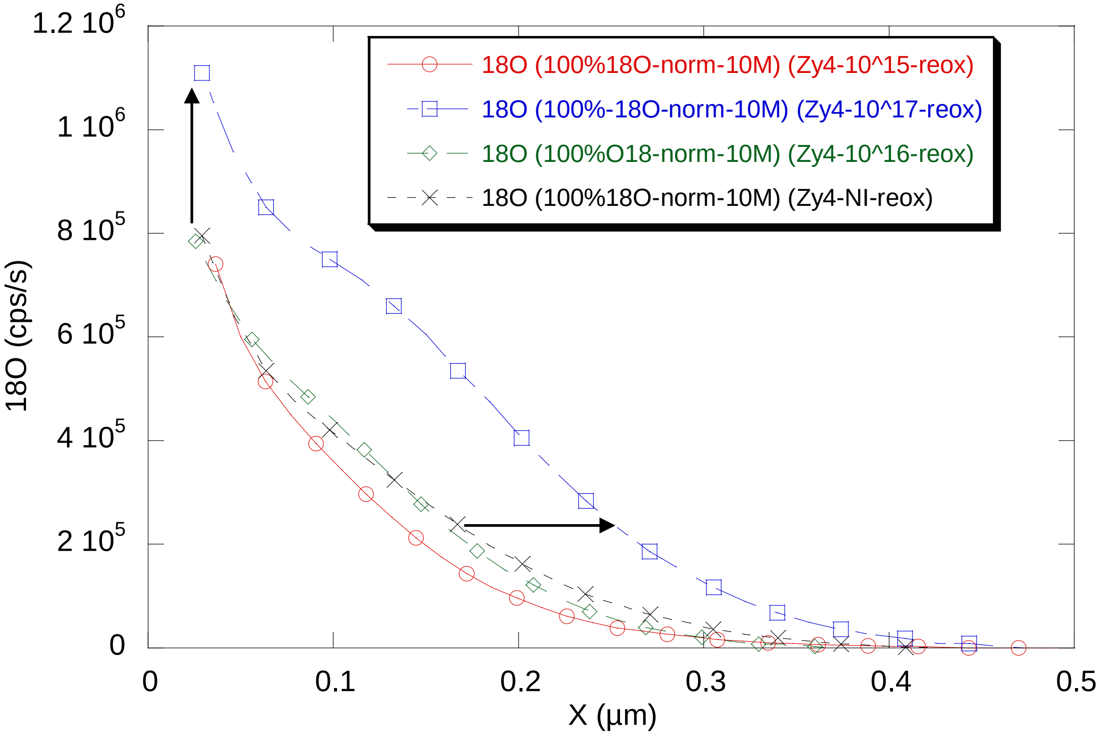
⇨ **dpa range : 2.10^{-3} => 2.10^{-1}**
⇨ **% of vacancies : 0.07 => 7**
⇨**Large range of irradiation damage**

Step 3 : hydrogen implantation measured by SIMS analyses



⇨**Simulations consistent with the SIMS profiles of hydrogen implantation**

Step 5 : SIMS profiles of oxygen 18 after Zy4 irradiation



- $C_{O18\text{-}surf}$: significant increase for the highest fluence
- D_{a_O18} : significant increase for the highest fluence

1. $\Phi \leq 10^{16}$ H^+/cm^2 : no strong impact on the oxygen 18 diffusion rate
2. $\Phi > 10^{16}$ H^+/cm^2 : significant increase on the oxygen 18 diffusion rate

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Step 5 : Quantification of the irradiation impact on the diffusion flux

⇨ estimation of the diffusion coefficient and the diffusion flux from the SIMS profiles

N sample	**68a**	**66a**	**67a**	**69a**
Fluence (ions/cm²)	-	**10^{15}**	**10^{16}**	**10^{17}**
$D_{a\text{-}O}$ (cm²/s)	$1.1.10^{-15}$	$0.9.10^{-16}$	$1.3.10^{-15}$	**$2.2.10^{-15}$**
$C_{O18\text{-}e}/C_{O18\text{-}e}(NI)$	1	1.05	1.05	**1.4**
J/J_{NI}	1	0.9	1.4	**3.1**

⇨ Highest dose : increase around 40% of the oxygen_18 surfacic concentration but also a factor 2 of the diffusion coefficient
⇨ Results consistent with our predictions

⇨ Results confirmed by irradiation experiments with helium ions

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Conclusions and perspectives:

⇒ Localised irradiation :

- significant increase of the oxygen diffusion flux in the oxide layer formed on Zy4 beyond a certain dose ranging from 0.05 to 0.1 dpa
- agreement with the working hypothesis concerning the irradiation impact on the corrosion rate of Zy4
- a tool to better understand oxidation mechanisms or to specify the rate limiting step of a corrosion process

⇒ perspectives : uniform damage distribution