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CIMTEC 2018

8th Forum on New Materials

Helium precipitation study in UO₂ by Transmission Electron Microscopy

A. Michel^{1,*}, G. Carlot¹, C. Sabathier¹, C. Onofri¹, M. Dumont² and
M. Cabie³

1. CEA / DEN / DEC, Saint Paul Lez Durance, France

2. IM2NP – UMR CNRS 7334 – Aix-Marseille Université, Marseille, France

3. CP2M – Aix-Marseille Université, Marseille, France

** adrien.michel2@cea.fr*

PERUGIA, ITALY – 14TH JUNE 2018

INTRODUCTION – SPENT NUCLEAR FUEL



In-pile irradiation

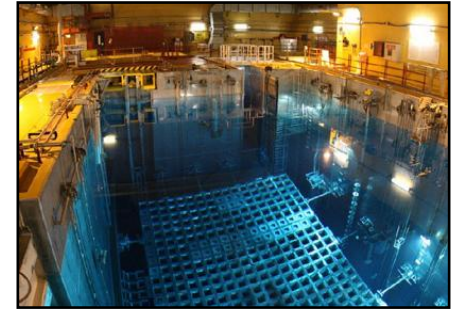


Fission products

Irradiation damages

Bubbles of fission gases

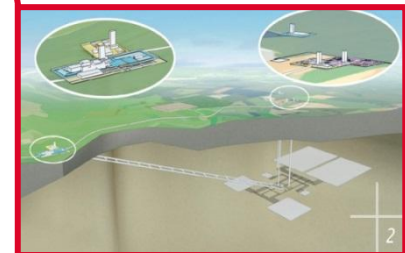
Microstructural changes



Management of spent fuel

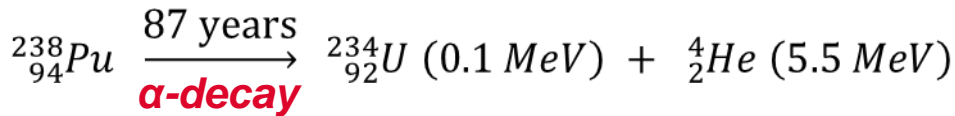


**Reference scenario :
Reprocessing**



**Optional scenario :
Direct disposal**

Direct disposal of spent nuclear fuel in deep geological layer



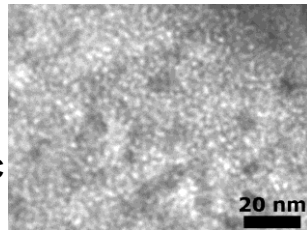
Microstructure alteration and/or pellet damaging

- Impact of helium on the microstructure evolution of the spent fuel
- To supply theoretical models of long time behaviour for spent fuel

LITERATURE ON HELIUM PRECIPITATION IN FUEL

| | Authors | Fuel type | Implantation | Annealing conditions | Bubble size (nm) | Bubble density (b.m ⁻³) |
|---------------------------|------------------|--|--|--|----------------------------|---|
| Implanted materials | Satonnay et al. | UO ₂ single crystal | 7 keV – 7.10 ¹⁵ at.cm ⁻² - 1 at. % | 600°C | ~ 25 | / |
| | Sabathier et al. | Polycrystalline UO ₂ | 7 keV - 7.10 ¹⁵ at.cm ⁻² - 1 at. % | T° > 500°C | No bubbles | / |
| | Sabathier et al. | Polycrystalline UO ₂ | 500 keV – 1.10 ¹⁶ – 0.3 at. % | 900°C 0min 1000°C 0min 1000°C 30min 1000°C 1h | ~ 1 2.7 1.5 - 2 3 | / 4.10 ²³ 1.10 ²⁴ 1.10 ²⁴ |
| Self-irradiated materials | Wiss et al. | (U _{0,9} ²³⁸ Pu _{0,1})O ₂ | / | > 600°C | 1 | / |
| | Talip et al. | (U _{0,9} ²³⁸ Pu _{0,1})O ₂ | / | 1130°C 1h 1530°C 3h | 1 - 2 5 - 6 | / |

TEM observation of helium bubbles in 500 keV He-implanted UO₂ (10¹⁶ at.cm⁻²) and annealed 30 min at 1000°C



→ Only few results on helium precipitation in oxide fuels and scattered results

Helium precipitation in UO₂ and (U,Pu)O₂ matrices

UO₂

Separated effects study:

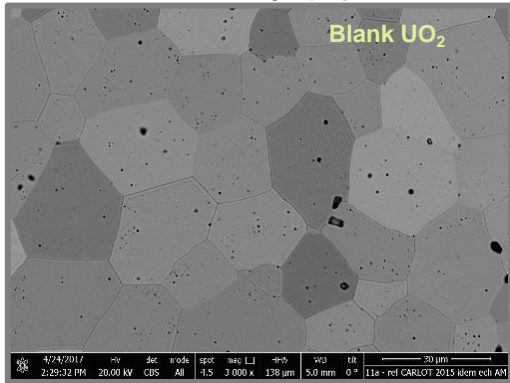
*Implantation - Irradiation – Temperature –
Fine characterization : TEM*



Size and density characterization of helium bubbles populations in disposal conditions

EXPERIMENTAL APPROACH

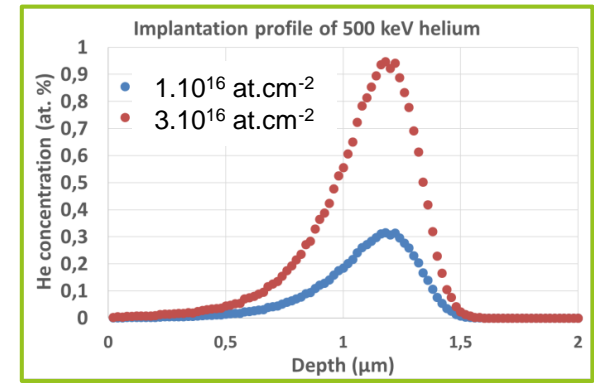
SEM micrography



Depleted UO₂ disks



SRIM calculations



Helium implantation
500 keV
 2 fluences 1.10^{16} and 3.10^{16} at.cm⁻²

In-situ annealing

| Temperature (°C) | Time (h) |
|------------------|----------|
| 200 | 5,7 |
| 400 | 10,3 |
| 600 | 6,5 |

RT°
 Ex-situ annealing

| Temperature (°C) | Time (h) |
|------------------|----------|
| 600 | 1 |
| 600 | 6 |
| 800 | 1 |

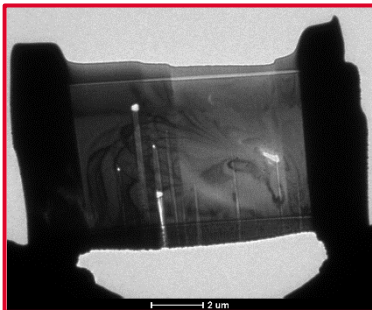
FIB preparation

**Transmission Electron
 Microscopy (TEM)**

FEI Tecnai G2
 Spatial resolution : 0.27 nm

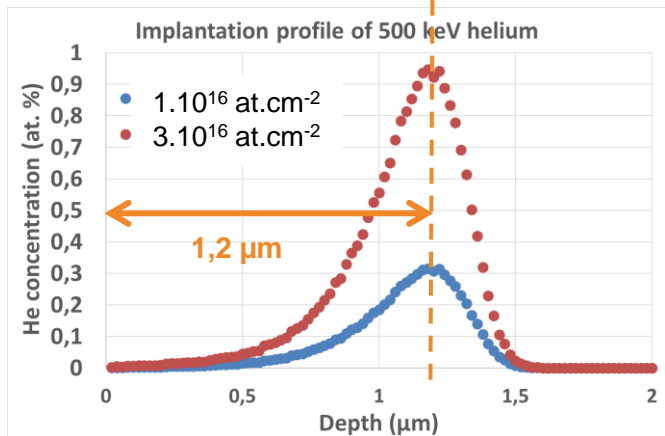
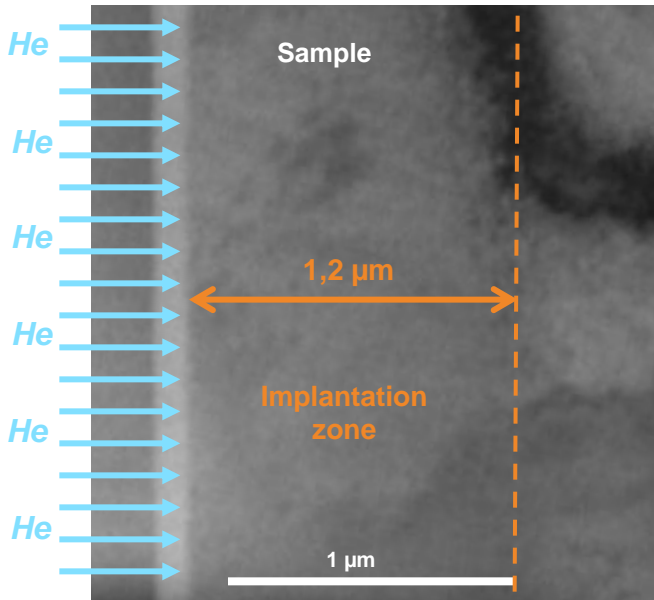
 FEI TITAN
 Spatial resolution : 0.1 nm

FIB cross section



TEM OBSERVATIONS

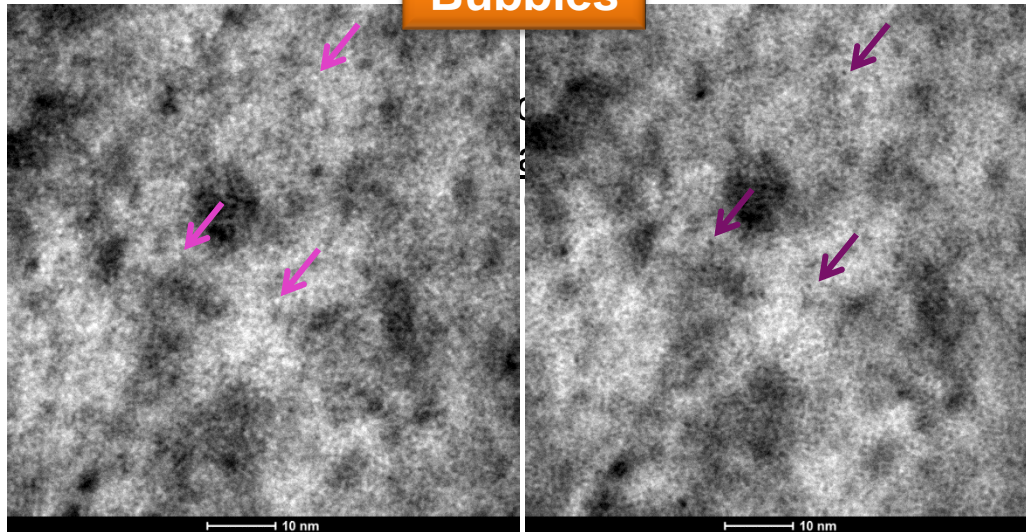
600°C and 3.10^{16} at.cm⁻² implanted sample



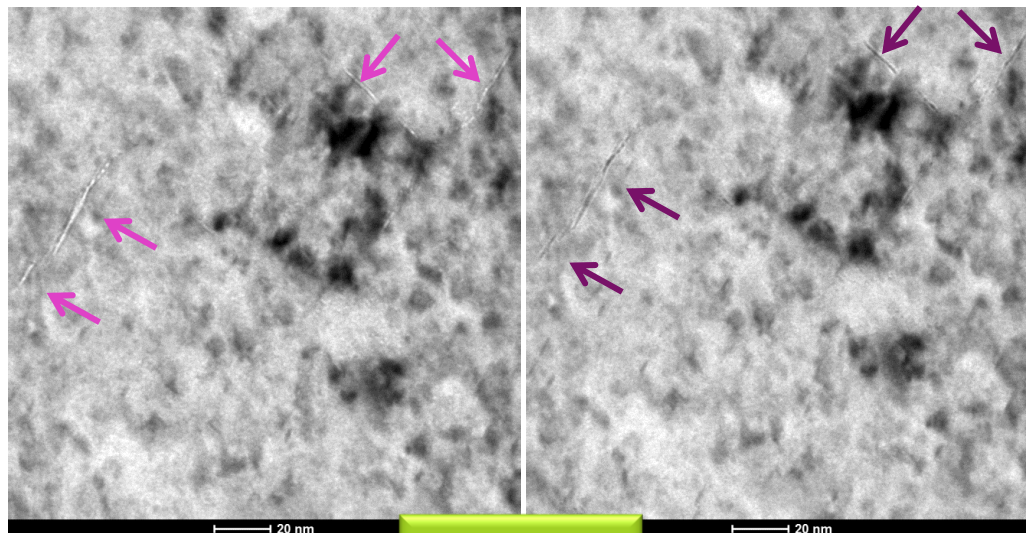
Under-focused image

Bubbles

Over-focused image



Condition of observation : white/black contrasts for under/over focused

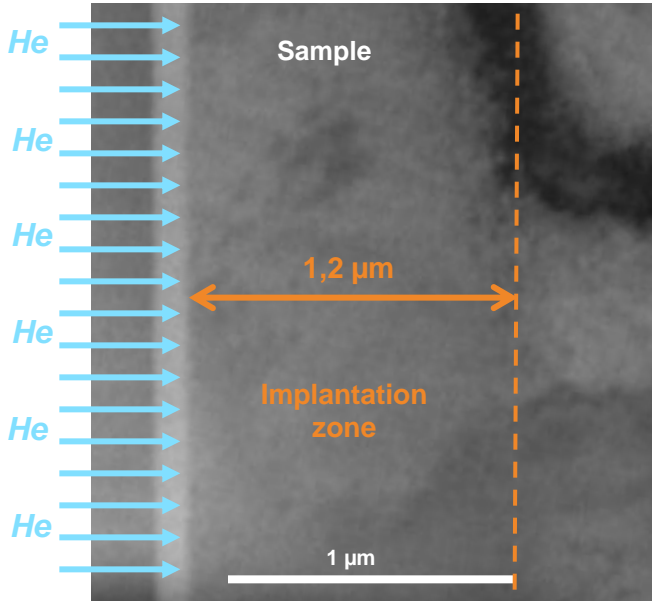


Under-focused image

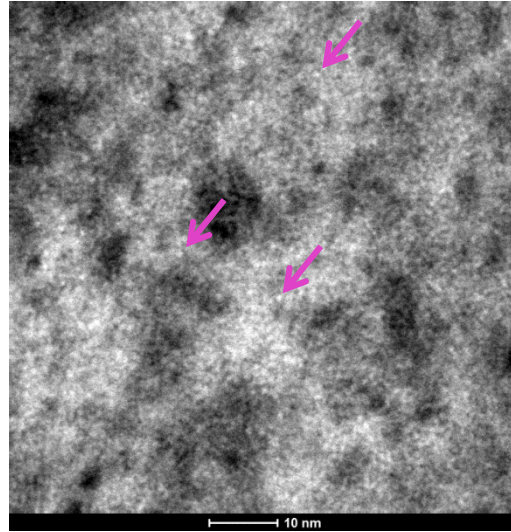
Platelets

Over-focused image

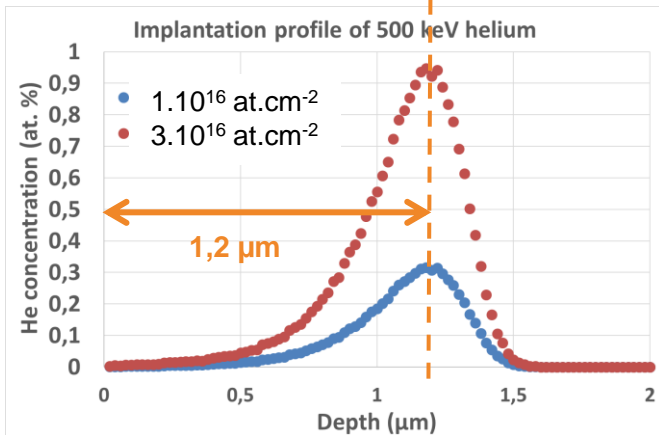
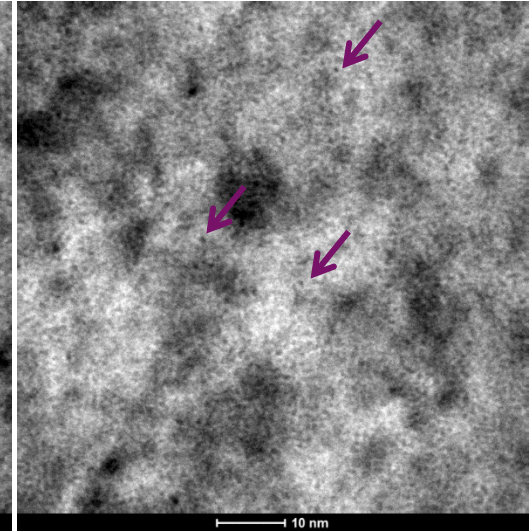
600°C and $3 \cdot 10^{16}$ at.cm⁻² implanted sample



Under-focused image



Over-focused image



| Annealing | Fluence (at.cm ⁻²) | Temperature (°C) | Time (h) | Bubbles |
|-----------|--------------------------------|------------------|----------|------------|
| In-situ | $1 \cdot 10^{16}$ | 200 | 4,4 | No |
| | | 400 | 2,3 | No |
| | | 600 | 1,8 | Yes |
| | $3 \cdot 10^{16}$ | 200 | 5,7 | No |
| | | 400 | 10,3 | No |
| | | 600 | 6,5 | Yes |

Bubbles are observed in the implantation zone for 600°C implantations at $1 \cdot 10^{16}$ and $3 \cdot 10^{16}$ at.cm⁻²

Images do not permit to know if there are bubbles or not for the other conditions

Method : « simply sight count »



Counts of all bubbles that appear in both images (under- and –over focused)

| Implantation conditions | Observation depth (μm) | He concentration (at.%) | Damages rate (dpa) | Bubble density (b.m^{-3}) <i>For 100 nm thick</i> | Diameter (nm) | Number of bubbles |
|---------------------------------|-------------------------------------|-------------------------|--------------------|---|-----------------|-------------------|
| $1.10^{16} - 600^\circ\text{C}$ | 0.1 | 0.0023 | 0.02 | $(7.5 \pm 6.0) \cdot 10^{21}$ | 0.58 ± 0.58 | 4 |
| $1.10^{16} - 600^\circ\text{C}$ | 0.8 | 0.072 | 0.12 | $(2.6 \pm 1.5) \cdot 10^{22}$ | 0.91 ± 0.53 | 14 |
| $3.10^{16} - 600^\circ\text{C}$ | 0.1 | 0.0069 | 0.06 | $(1.5 \pm 1.0) \cdot 10^{22}$ | 0.79 ± 0.57 | 8 |
| $3.10^{16} - 600^\circ\text{C}$ | 0.1 | 0.0069 | 0.06 | $(1.1 \pm 0.8) \cdot 10^{22}$ | 0.85 ± 0.63 | 6 |
| $3.10^{16} - 600^\circ\text{C}$ | 1.4 | 0.23 | 0.12 | $(4.5 \pm 2.3) \cdot 10^{22}$ | 0.89 ± 0.47 | 24 |
| $3.10^{16} - 600^\circ\text{C}$ | 1.2 | 0.92 | 0.81 | $(3.0 \pm 1.9) \cdot 10^{22}$ | 0.86 ± 0.57 | 9 |
| $3.10^{16} - 600^\circ\text{C}$ | 1.2 | 0.92 | 0.81 | $(2.4 \pm 1.4) \cdot 10^{22}$ | 0.85 ± 0.52 | 13 |

Bubbles density of about 10^{22} b.m^{-3}

Maximum size of 1 nm

→ No evolution of the diameter and of the bubble density as a function of the depth or of the helium concentration

Very low statistics

Important quantity of defects → Addition of parasite contrast → Insufficient image quality

Need to improve the observations

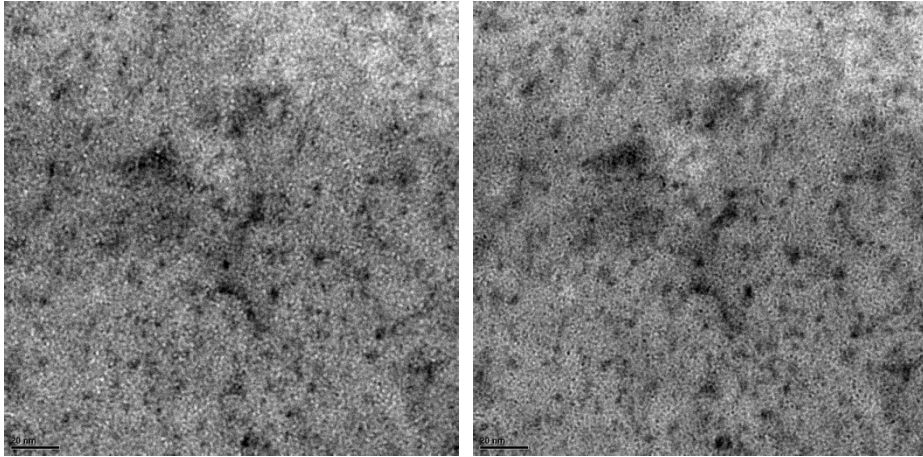
→ Complicated image analysis AND high measurement uncertainties

Need to improve the image analysis method

Observations with a TEM FEI TITAN

« Simply sight count » method :

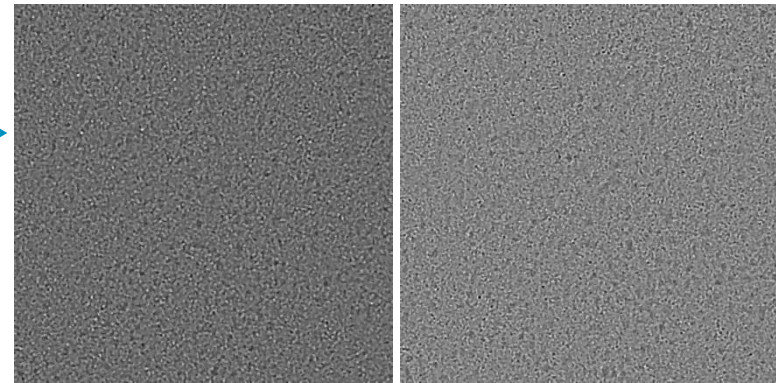
72 counted bubbles so $(5.3 \pm 2.2) \cdot 10^{22}$ b.m⁻³ for density and 1.43 ± 0.90 nm for the mean diameter



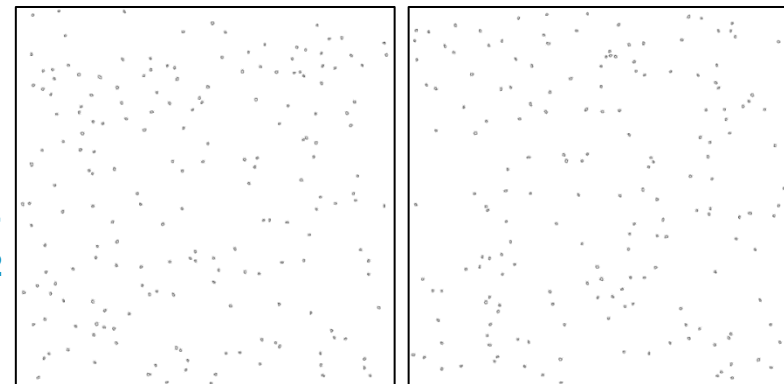
3.10¹⁶ at.cm⁻² – 600°C implanted sample after an 1h/400°C annealing on FIB cross section

Development of a new method using ImageJ software :

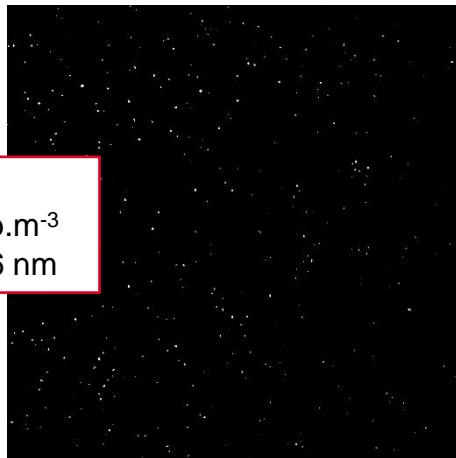
Correction of magnification as a function of focus
Treatment and alignment of images



Thresholding of images and particle analysis



Covering of 2 images



130 counted objects
Density : $(9.3 \pm 3.6) \cdot 10^{22}$ b.m⁻³
Mean diameter : 1.4 ± 0.86 nm

- Comparison of both methods :

| | Bubbles number | Density (b.m ⁻³) | Mean diameter (nm) |
|---------------------------|----------------|-------------------------------|--------------------|
| Simply sight count method | 72 | $(5.3 \pm 2.2) \cdot 10^{22}$ | 1.43 ± 0.90 |
| Method using ImageJ | 130 | $(9.3 \pm 3.6) \cdot 10^{22}$ | 1.40 ± 0.86 |

→ Difference on number of counted objects between the 2 methods but not on the mean diameter

Advantages

- No dependence of the user on the results
- Take into account the difference of alignment of the images
- Treatment and thresholding steps enable to free itself from defects problems
- Count rate more important

Optimization

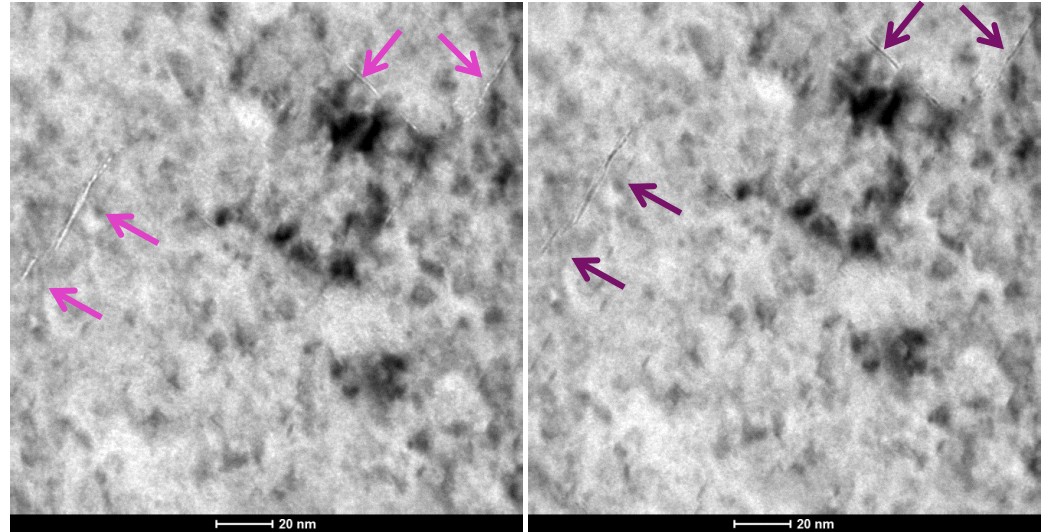
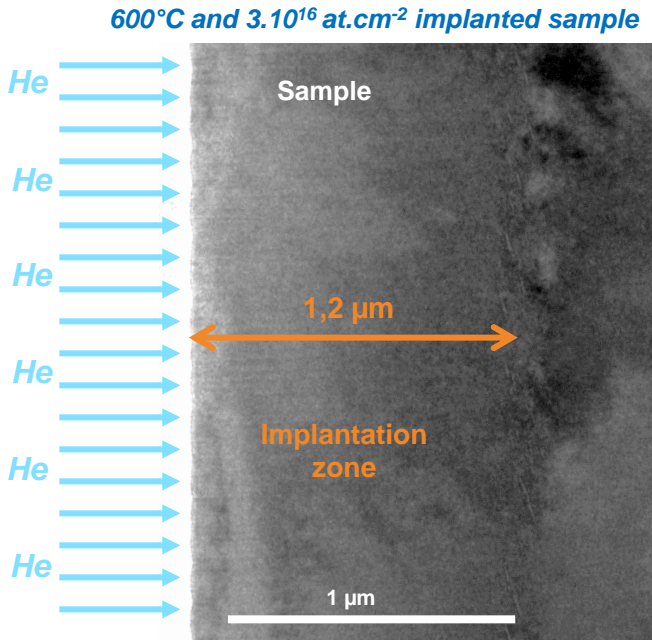
- Implement automatic fonctions to detect the particles
- Use of macros to automate the method

⇒ Observations of the samples with the more powerful TEM

⇒ Optimization step of the ImageJ method

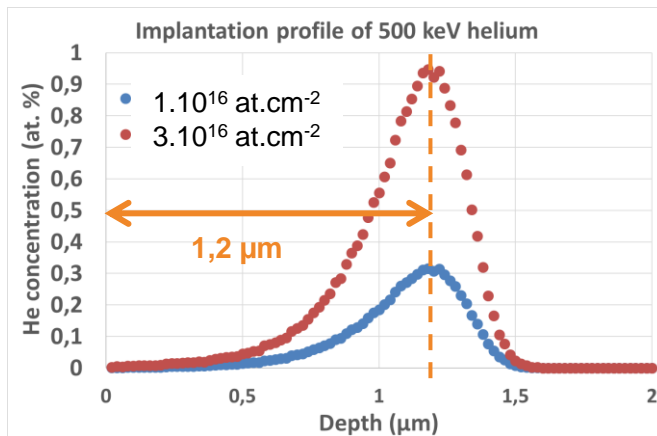
⇒ Use the ImageJ method to characterize helium bubbles improving values and measurements uncertainties

On 200 nm centered at the depth of the implantation peak



Under-focused image

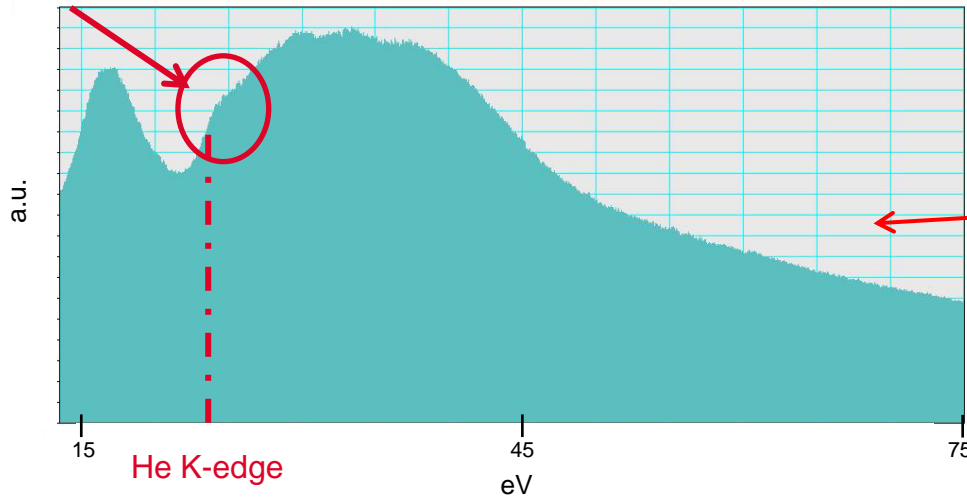
Over-focused image



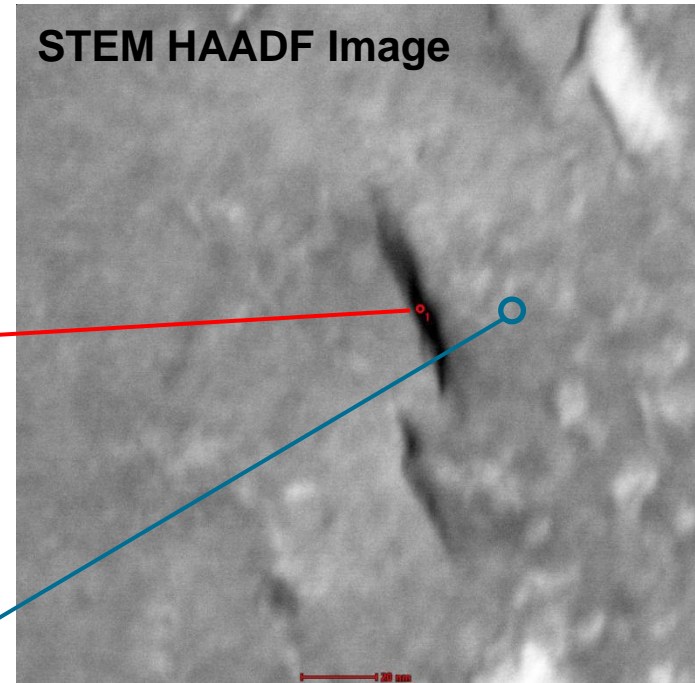
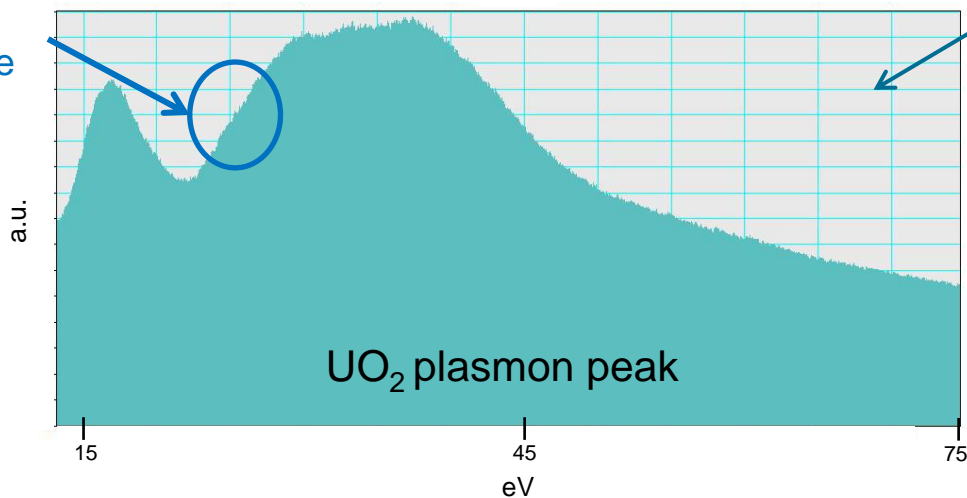
| Annealing | Fluence (at.cm ⁻²) | Temperature (°C) | Time (h) | Platelets |
|-----------|--------------------------------|------------------|------------|------------|
| In-situ | 1.10 ¹⁶ | 200 / 400 / 600 | / | No |
| | 3.10¹⁶ | 200 | 5,7 | No |
| | | 400 | 10,3 | No |
| | | 600 | 6,5 | Yes |
| Ex-situ | 1.10 ¹⁶ | 800 | 1 | No |
| | 3.10¹⁶ | 600 | 1 | No |
| | | 600 | 6 | Yes |
| | | 800 | 1 | Yes |

EELS spectrum

Increase observed at the level of the He K-edge



No increase



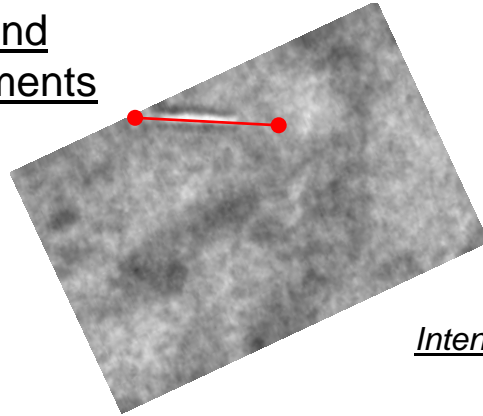
$3 \cdot 10^{16} \text{ at.cm}^{-2}$ and 600°C implanted sample

For a diluted gas, the K threshold is equal to 21.218 eV [1]

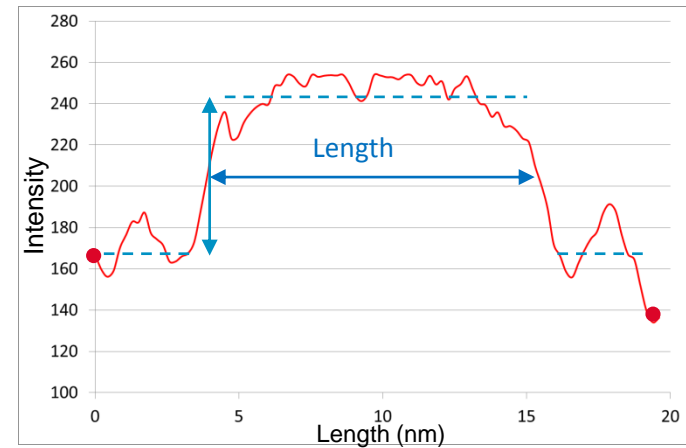
It can be shifted to the high value (blue shift) when He density increases [2]

[1] Kuhn, Atomic spectra (1962) 132
[2] Fréchar et al. JNM 393 (2009) 102

Step 1 : Length and thickness measurements



Intensity profile



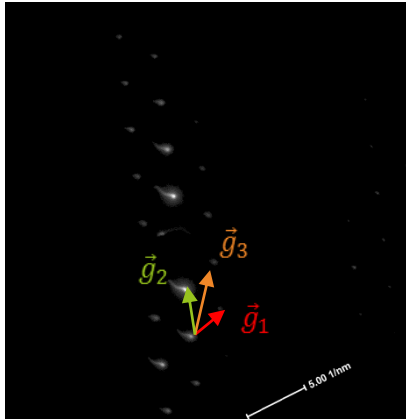
| Implantation conditions (°C – at.cm ⁻²) | Bulk annealing | Platelet length | | Platelet thickness | | Number of platelets | Surface density of platelets (platelets.m ⁻²) <i>On the layer of 200 nm thick</i> |
|--|----------------|---------------------|---------------------|------------------------|------------------------|---------------------|---|
| | | Minimum length (nm) | Maximum length (nm) | Minimum thickness (nm) | Maximum thickness (nm) | | |
| 600 – 3.10 ¹⁶ | No | 17 ± 3 | 76 ± 15 | 0.4 ± 0.1 | 1.1 ± 0.5 | 12 | (9.3 ± 2.7) .10 ¹³ |
| 600 – 3.10 ¹⁶ | No | 5 ± 1 | 49 ± 8 | 0.6 ± 0.1 | 3.9 ± 0.8 | 25 | (8.4 ± 1.7) .10 ¹³ |
| RT – 3.10 ¹⁶ | 800°C / 1 h | 16 ± 3 | 77 ± 15 | 0.5 ± 0.1 | 2.1 ± 0.4 | 17 | (3.7 ± 0.9) .10 ¹³ |
| RT – 3.10 ¹⁶ | 600°C / 6 h | 6 ± 1 | 93 ± 18 | 0.4 ± 0.1 | 0.9 ± 0.2 | 11 | (1.4 ± 0.4) .10 ¹⁴ |

Length included between a few nanometers and around a hundred of nanometers

Thickness of about a few nanometers

Density of about 10¹³/10¹⁴ platelets.m⁻²

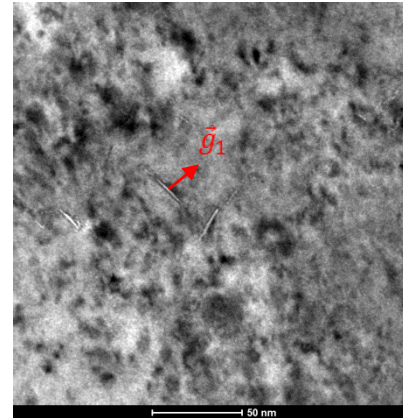
Step 2 : Diffraction patterns indexation



Interreticular distances measurements :

$$\begin{aligned} \vec{g}_1 &= \langle 1 \ 1 \ 1 \rangle \\ \vec{g}_2 &= \langle 0 \ 0 \ 2 \rangle \\ \vec{g}_3 &= \langle 1 \ 1 \ 3 \rangle \end{aligned}$$

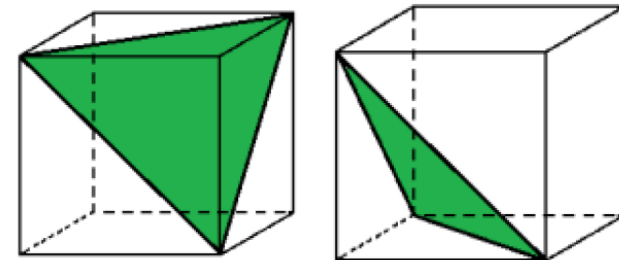
Step 3 : Search of habit planes



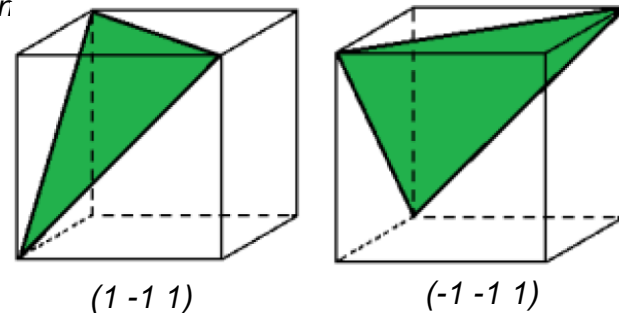
Platelets that are perpendicular to a diffraction vector \vec{g} lie in the habit plan that corresponds to \vec{g} . Here, for example, the platelet lie in the plane $\{1 \ 1 \ 1\}$

| Implantation conditions (°C – at.cm ⁻²) | Annealing | Platelets number | Habit plane |
|---|-------------|------------------|-------------|
| 600 – 3.10 ¹⁶ | No | 25 | {1 1 1} |
| | | | {1 1 1} |
| RT – 3.10 ¹⁶ | 800°C / 1 h | 17 | {1 1 1} |
| RT – 3.10 ¹⁶ | 600°C / 6 h | 11 | {1 1 1} |

→ It seems that platelets preferentially appear in {1 1 1} type habit plans.



4 possible variants of the {1 1 1} habit plan in UO₂ :



CONCLUSION ON HELIUM PRECIPITATION IN UO_2

Bubbles

- Presence of helium bubbles for 600°C implantations for two fluences 1.10^{16} and 3.10^{16} at.cm⁻² : maximum size of 1 nm and a density of about 10^{22} b.m⁻³
- Difficulties to highlight the influence of temperature and helium concentration on their features

Development
optimized method
of TEM images



To characterize helium bubbles populations with improving values and uncertainties

SAXS
measurements



To obtain complementary characterizations on helium bubbles features

Platelets

- Presence of helium platelets for an implantation in temperature or a post-implantation annealing at 600°C or 800°C for the higher fluence 3.10^{16} at.cm⁻²
- Effect of annealing time on the presence or not of platelets.
- Helium platelets preferentially form in {1 1 1} type habit plans

Complementary
TEM observations



To determine precisely habit planes with different variants



To study the intergranular behaviour of platelets

He precipitation in UO_2

Influence of fission
gases bubbles

Influence of
irradiation damages

Outlook

He precipitation in $(\text{U,Pu})\text{O}_2$

TEM characterization on MOX
containing radiogenic He

Thank you for your attention !

Contact :
adrien.michel2@cea.fr