



Helium precipitation study in UO₂ by Transmission Electron Microscopy

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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

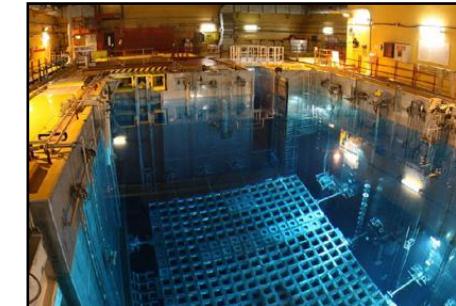
PERUGIA, ITALY – 14TH JUNE 2018

INTRODUCTION – SPENT NUCLEAR FUEL



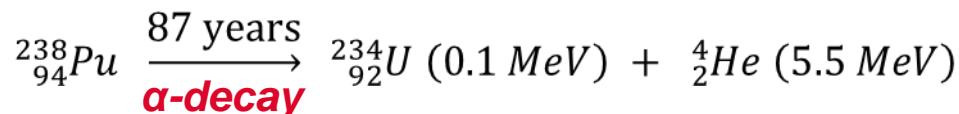
In-pile irradiation

- Fission products
- Irradiation damages
- Bubbles of fission gases
- Microstructural changes



Management of spent fuel

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



Reference scenario :
Reprocessing

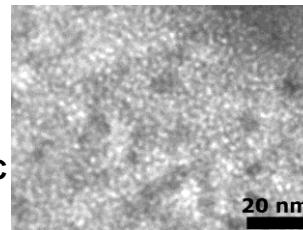


Optional scenario :
Direct disposal

LITERATURE ON HELIUM PRECIPITATION IN FUEL

	Authors	Fuel type	Implantation	Annealing conditions	Bubble size (nm)	Bubble density (b.m ⁻³)
Implanted materials	Sattonnay 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:

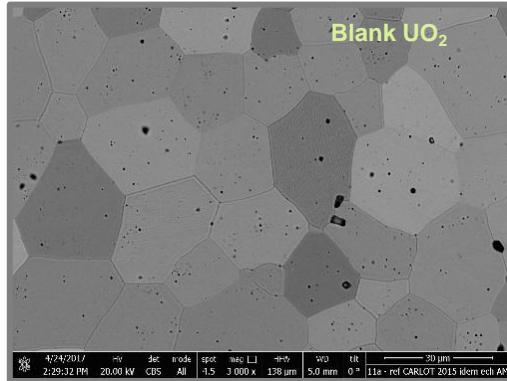
Implantation - Irradiation – Temperature – Fine characterization : TEM



Size and density characterization of helium bubbles populations in disposal conditions

EXPERIMENTAL APPROACH

SEM micrography



Depleted UO₂ disks



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

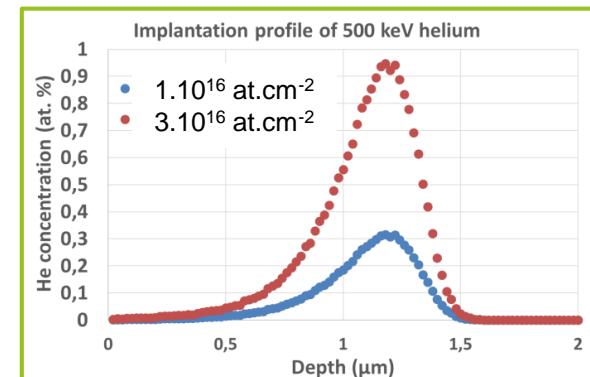
FIB cross section



FIB preparation

Transmission Electron Microscopy (TEM)

SRIM calculations



RT°

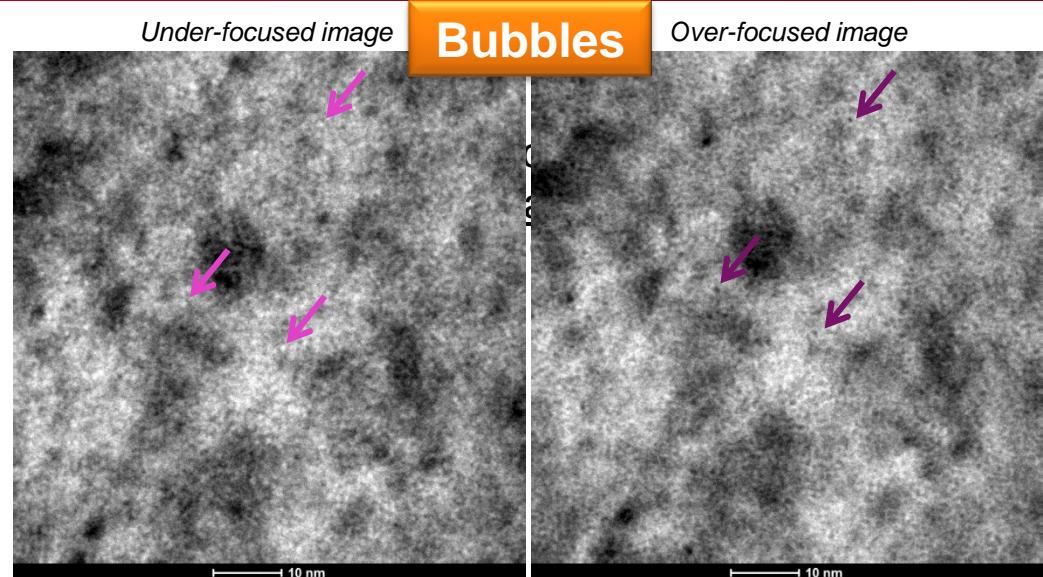
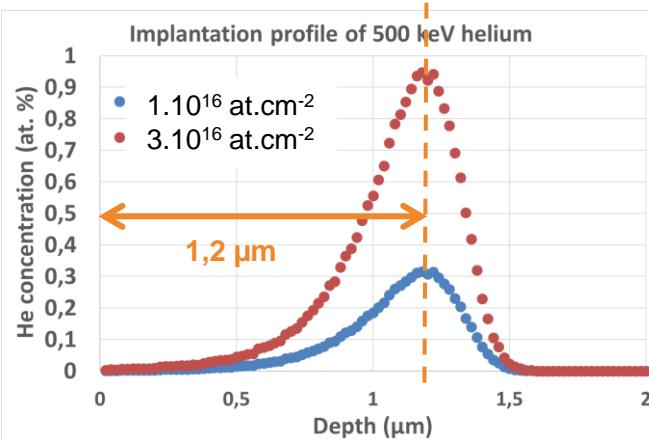
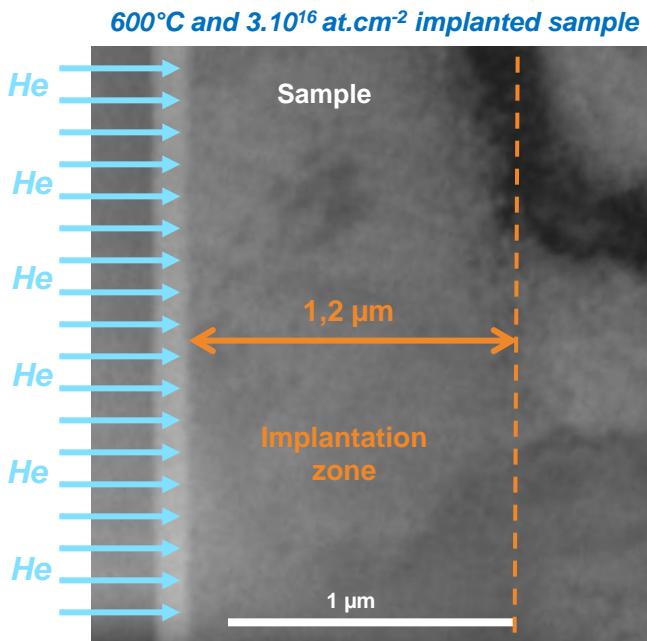
Ex-situ annealing

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

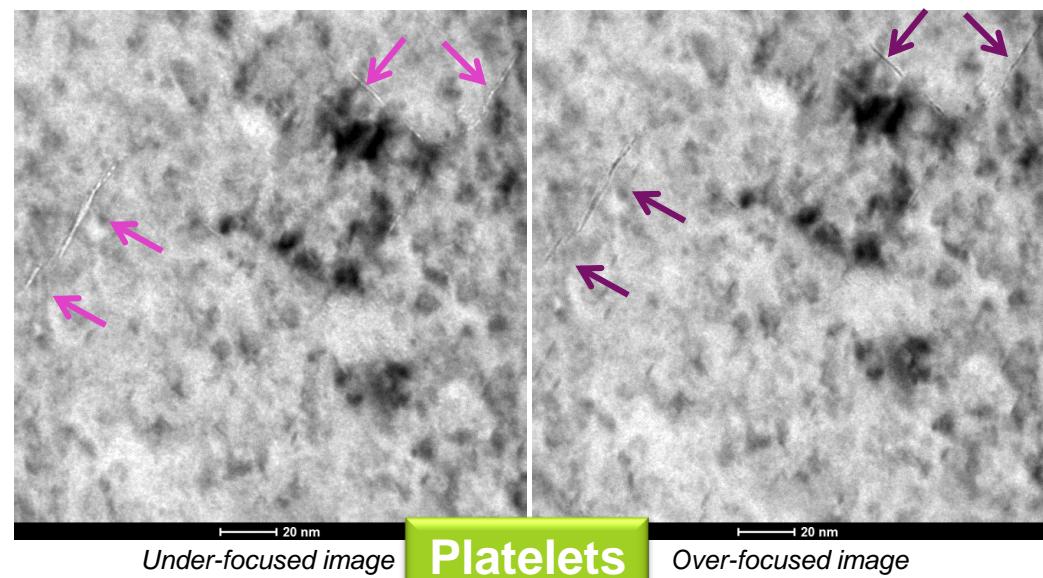
FEI Tecnaï G2
Spatial resolution : 0.27 nm

FEI TITAN
Spatial resolution : 0.1 nm

TEM OBSERVATIONS

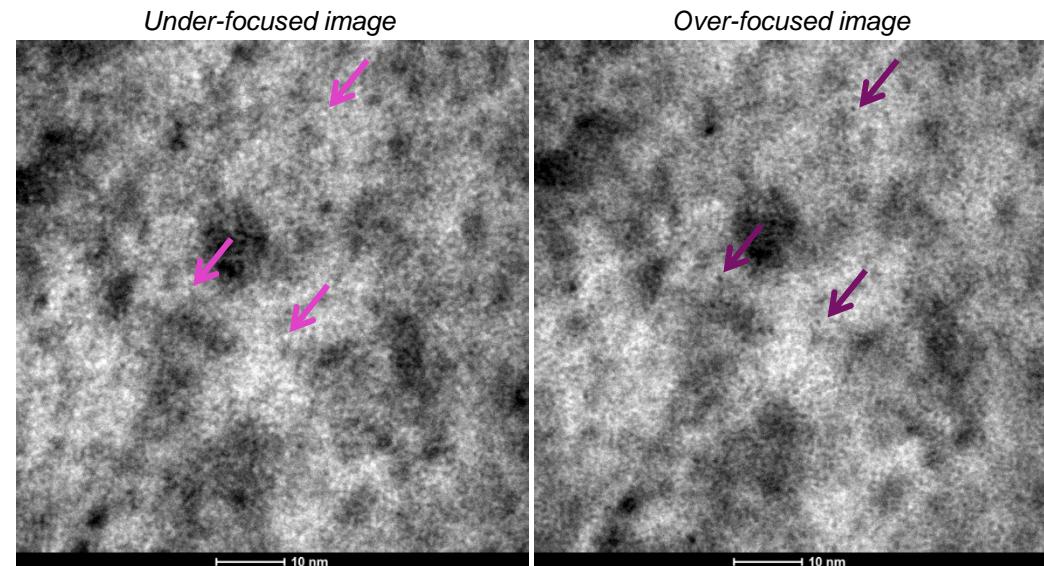
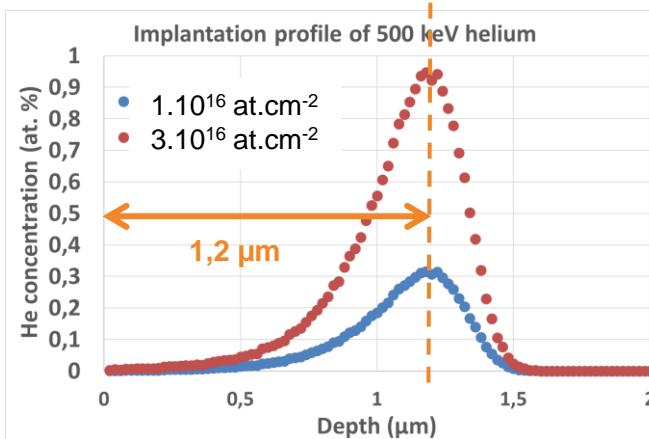
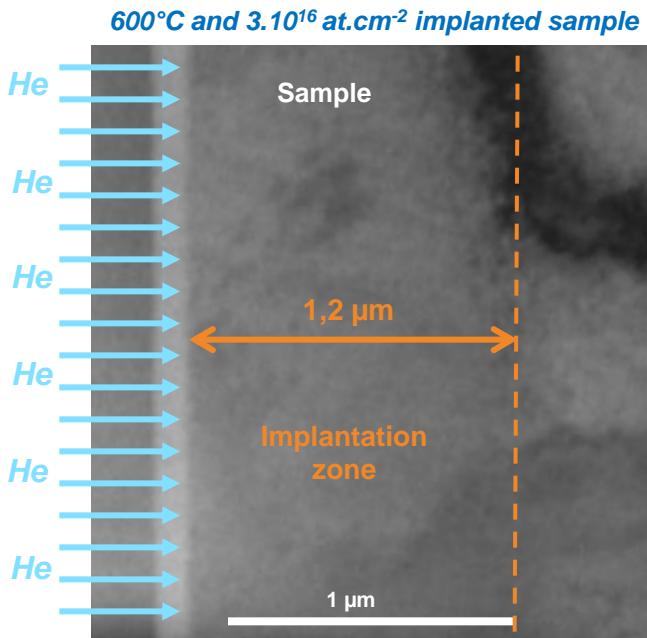


Condition of observation : white/black contrasts for under/over focused



CONDITIONS FOR OBSERVATIONS

Bubbles



Annealing	Fluence (at.cm ⁻²)	Temperature (°C)	Time (h)	Bubbles
In-situ	1.10 ¹⁶	200	4,4	No
		400	2,3	No
		600	1,8	Yes
	3.10 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 1.10^{16} and 3.10^{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}) For 100 nm thick	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

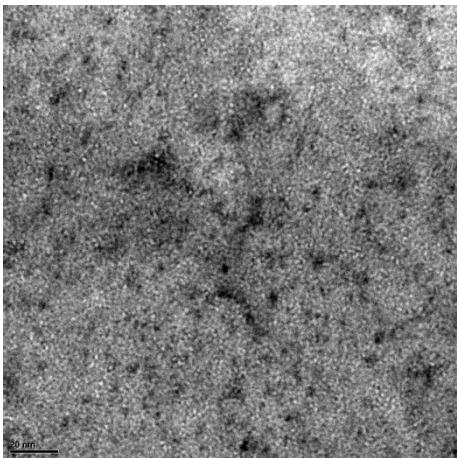
Need to improve the observations

→ Complicated image analysis AND high measurement uncertainties

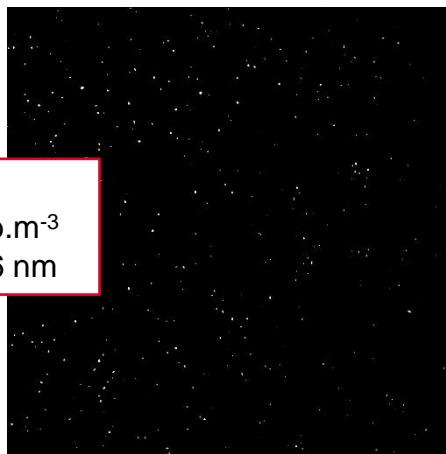
Need to improve the image analysis method

Observations with a TEM FEI TITAN**« Simply sight count » method :**

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



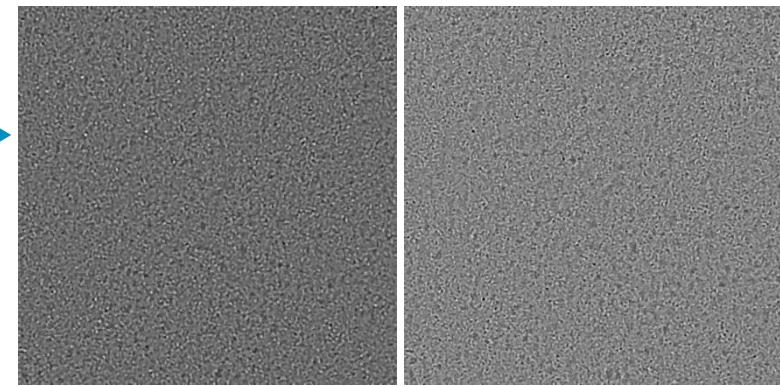
$3.10^{16} \text{ at.cm}^2 - 600^\circ\text{C implanted sample after an 1h/400^\circ\text{C annealing on FIB cross section}$



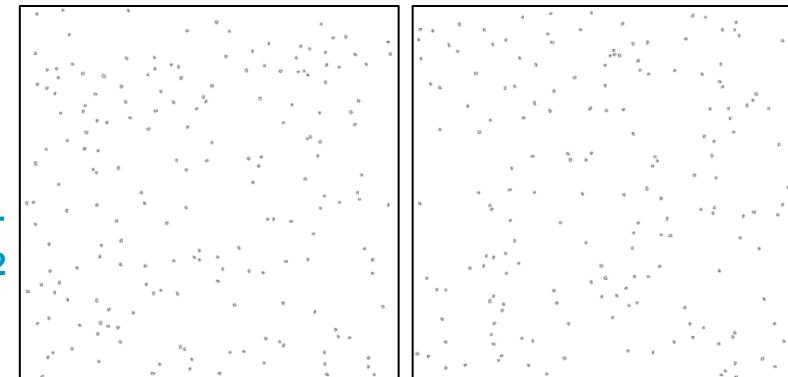
130 counted objects
 Density : $(9.3 \pm 3.6) \cdot 10^{22} \text{ b.m}^{-3}$
 Mean diameter : $1.4 \pm 0.86 \text{ nm}$

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

CONCLUSION ON THE RESULTS

Bubbles

- Comparison of both methods :

	Bubbles number	Density (b.m⁻³)	Mean diameter (nm)
Simply sight count method	72	(5.3 ± 2.2) .10 ²²	1.43 ± 0.90
Method using ImageJ	130	(9.3 ± 3.6) .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 functions to detect the particles
- Use of macros to automate the method



Observations of the samples with the more powerful TEM

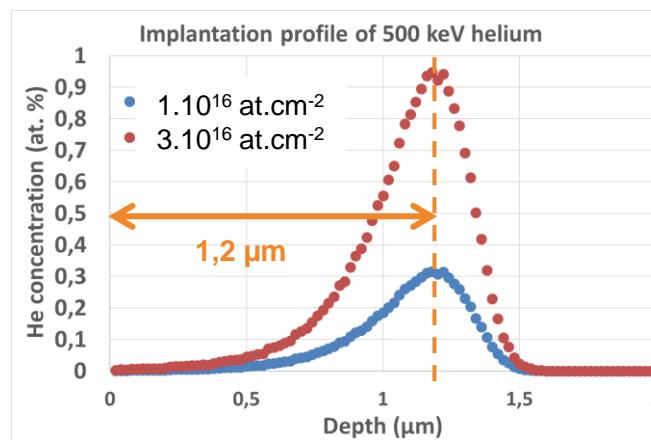
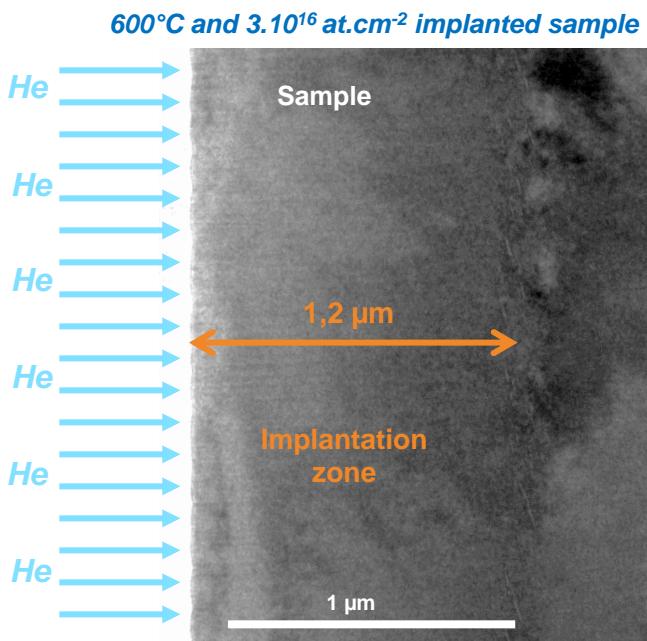


Optimization step of the ImageJ method

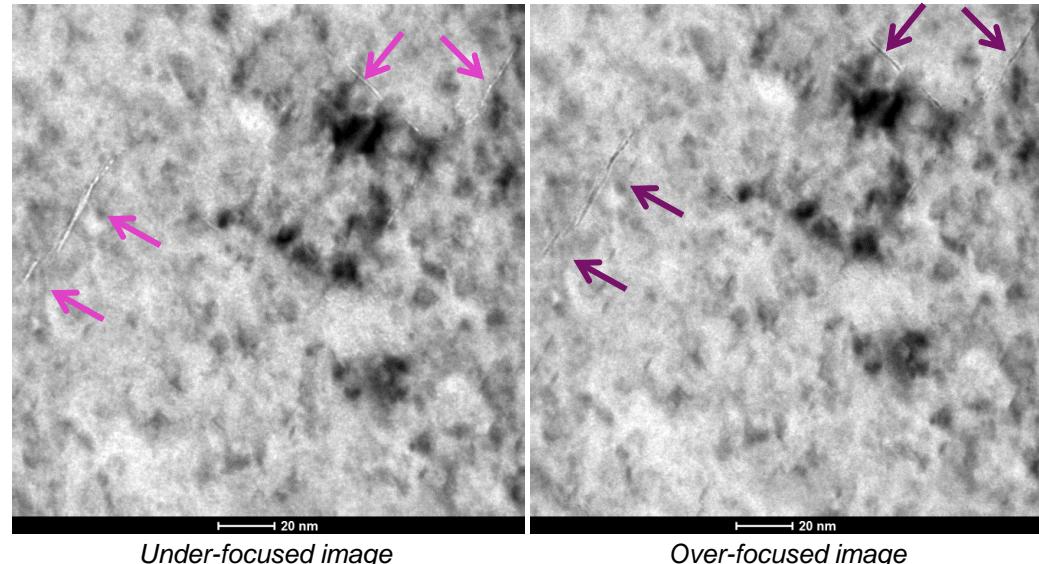


Use the ImageJ method to characterize helium bubbles improving values and measurements uncertainties

CONDITIONS FOR OBSERVATION

Platelets

On 200 nm centered at the depth of the implantation peak



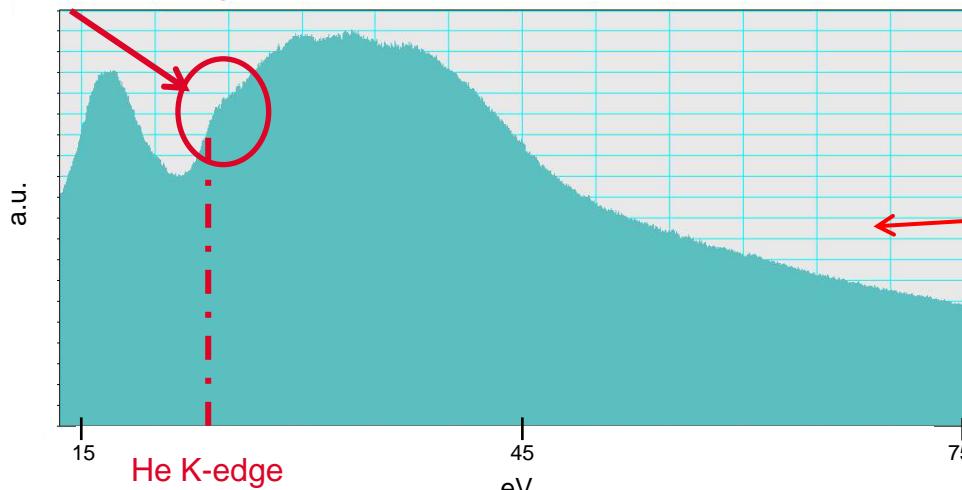
Annealing	Fluence (at.cm ⁻²)	Temperature (°C)	Time (h)	Platelets
In-situ	1.10 ¹⁶	200 / 400 / 600	/	No
	3.10¹⁶	200	5,7	No
		400	10,3	No
		600	6,5	Yes
Ex-situ	1.10 ¹⁶	800	1	No
	3.10¹⁶	600	1	No
		600	6	Yes
		800	1	Yes

EELS ANALYSIS

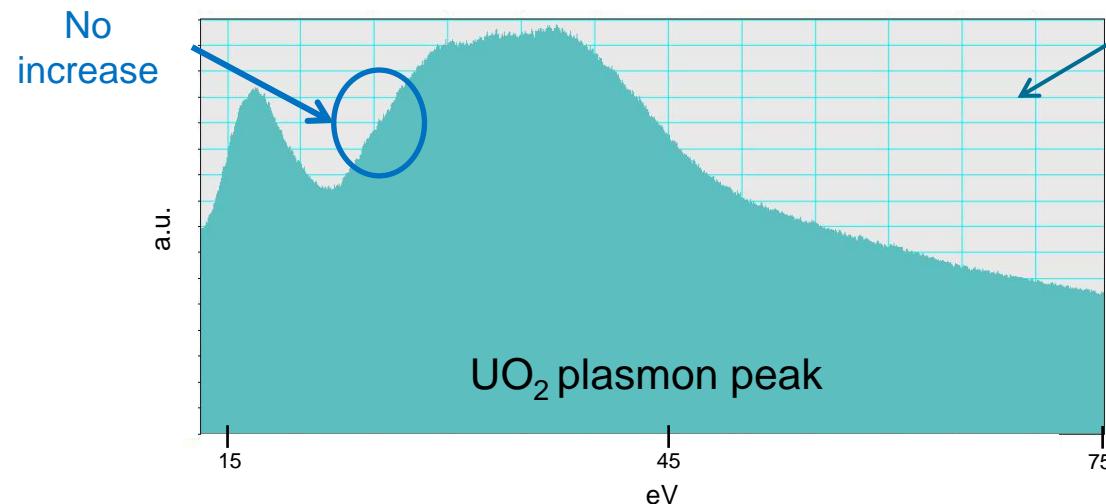
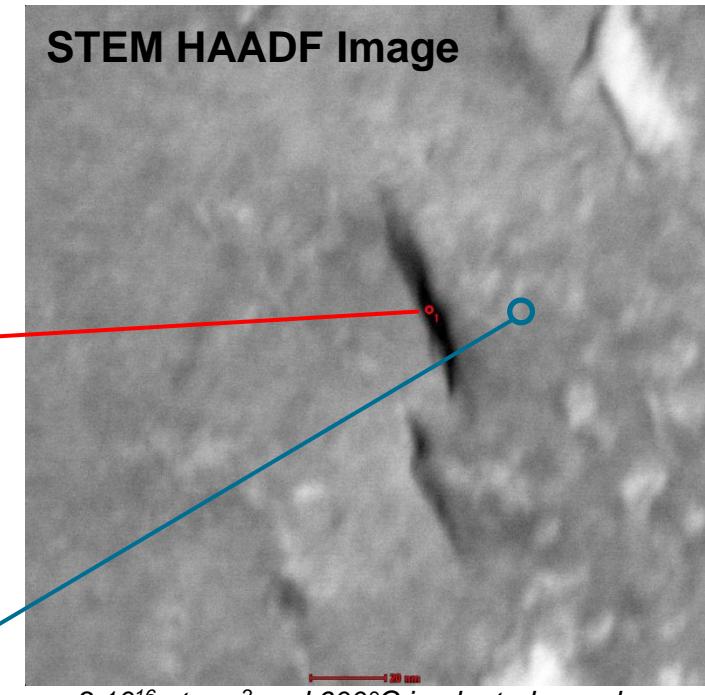
Platelets

EELS spectrum

Increase observed at the level of the He K-edge



STEM HAADF Image



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]

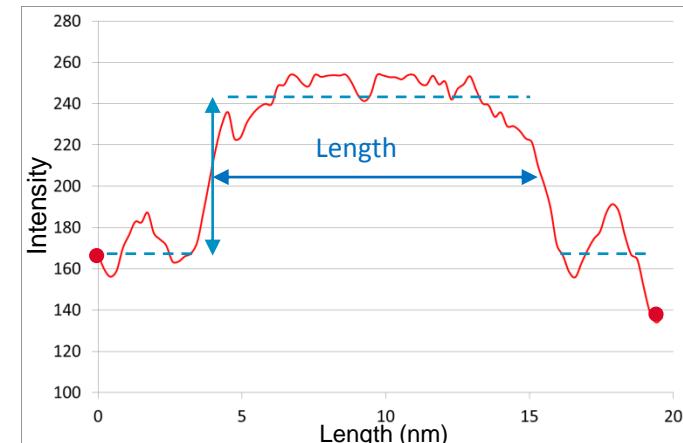
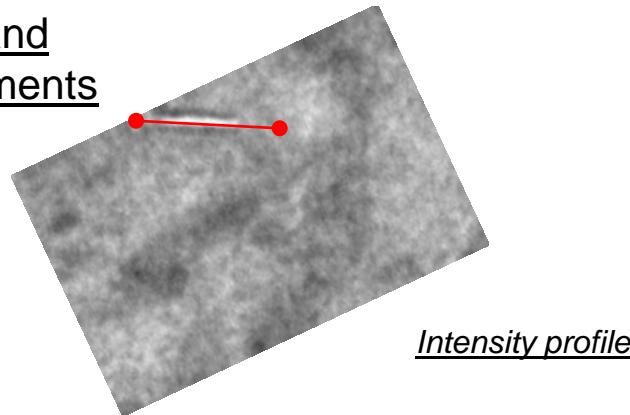
[1] Kuhn, Atomic spectra (1962) 132

[2] Fréchard et al. JNM 393 (2009) 102

ANALYSIS TEM IMAGES

Platelets

Step 1 : Length and thickness measurements



Implantation conditions (°C – at.cm ⁻²)	Bulk annealing	Platelet length		Platelet thickness		Number of platelets	Surface density of platelets (platelets.m ⁻²) On the layer of 200 nm thick
		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

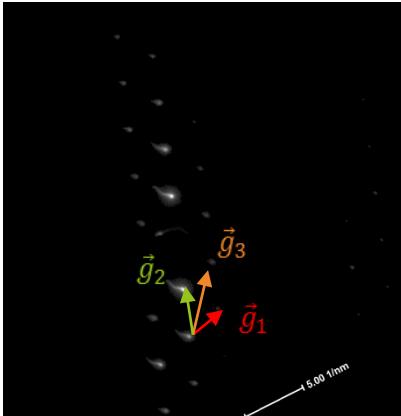
Thickness of about a few nanometers

Density of about 10¹³/10¹⁴ platelets.m⁻²

ANALYSIS TEM IMAGES

Platelets

Step 2 : Diffraction patterns indexation



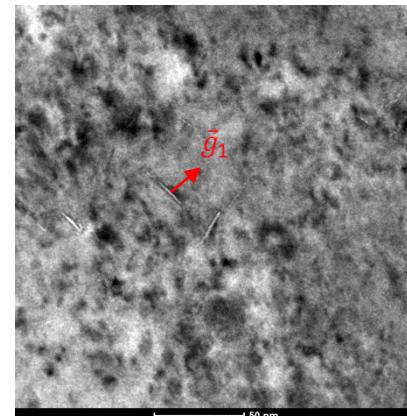
Interreticular distances measurements :

$$\vec{g}_1 = <1\ 1\ 1>$$

$$\vec{g}_2 = <0\ 0\ 2>$$

$$\vec{g}_3 = <1\ 1\ 3>$$

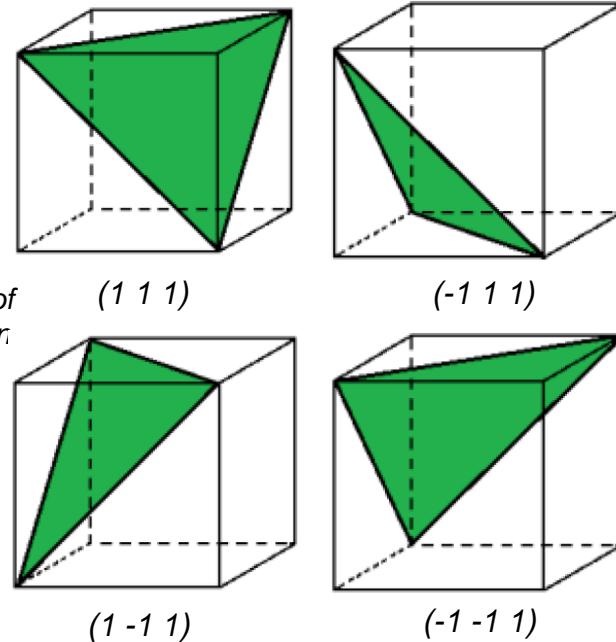
Step 3 : Search of habit planes



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 ($^{\circ}\text{C} - \text{at.cm}^{-2}$)	Annealing	Platelets number	Habit plane
600 – $3.\text{10}^{16}$	No	25	$\{1\ 1\ 1\}$
			$\{1\ 1\ 1\}$
RT – $3.\text{10}^{16}$	800°C / 1 h	17	$\{1\ 1\ 1\}$
RT – $3.\text{10}^{16}$	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 UO_2 :

CONCLUSION ON HELIUM PRECIPITATION IN UO₂

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 planes

Complementary TEM observations

→ To determine precisely habit planes with different variants
 → To study the intergranular behaviour of platelets

He precipitation in UO₂

Influence of fission gases bubbles

Influence of irradiation damages

Outlook

He precipitation in (U,Pu)O₂

TEM characterization on MOX containing radiogenic He

Thank you for your attention !

Contact :

adrien.michel2@cea.fr