The behaviour of fission products in uranium dioxide has been a focus of considerable experimental and theoretical attention in the nuclear industry. Xenon and krypton have attracted particular attention due to their high fission yields. During in-reactor irradiation of the nuclear fuel, rare gases are subject to several phenomena: diffusion and precipitation. These phenomena can have adverse consequences on the fuel physical and chemical properties and its in-reactor behavior. When released from the material they induce an increase in the fuel rod pressure detrimental to its integrity. A greater understanding of the mechanisms that underpin rare gas diffusion and precipitation should enable the development of models with a greater predictive capability and also make it possible to optimize fuel microstructures so as to increase the fuel element discharge burnup. The development of models for describing oxide behavior is hindered by the lack of experimental data available. The aim is to contribute to the understanding of the prevailing phenomena and generate sets of fundamental data necessary for modelling rare gas behaviour. The purpose of this work is to better understand the behavior of fission gases by identifying diffusion and bubble nucleation. To do this, studies involving separate effects have been established coupling ion irradiations/implantations with fine characterizations (Thermal Desorption Spectrometry and Transmission electron microscopy).

In order to analyse the mechanisms involved in rare gases diffusion, we carried out Thermal Desorption Spectrometry (TDS) measurements on the PIAGARA (Plateforme Interdisciplinaire pour l’Analyse des GAz Rares en Aquitaine) platform at CENBG laboratory in Bordeaux on UO$_2$ samples implanted at low fluence [Fig. 1]. The experiment involves heating a sample in a small furnace to induce rare gases movement and release and using mass spectrometry to monitor the amount of rare gases released as a function of time. Interpretation of the release experiments has enabled us to determine xenon and krypton diffusion coefficients in uranium dioxide.
Transmission electron microscopy (TEM) observations of UO$_2$ polycrystals irradiated in situ with 4 MeV Au ions were performed at room temperature (RT) to better understand the mechanisms of cavity and ultimately fission products nucleation in UO$_2$. Experiments were carried out at the JANNuS Orsay facility that enables in situ ion irradiations inside the microscope to be carried out. The majority of 4 MeV gold ions were transmitted through the thin foil, and the induced radiation defects were investigated by TEM. Observations showed that nano-void formation occurs at ambient temperature in UO$_2$ thin foils irradiated with energetic heavy ions under an essentially nuclear energy loss regime. The diameter and density of nano-objects were measured as a function of the gold irradiation dose at RT [Fig. 2]. A previous study [1] has also revealed a similar nano-object population after a Xe implantation performed at 390 keV at 870 K. The nano-object density was modelled using simple concepts derived from Classical Molecular Dynamics simulations. The results are in good agreement, which suggests a mechanism of heterogeneous nucleation induced by energetic cascade overlaps. This indicates that nano-void formation mechanism is controlled by radiation damage. Such nanovoids are likely to act as sinks for mobile fission products during reactor operation.

![Graph](image_url)

**Fig. 2:** Nano-void density evolution with Au irradiation at RT from TEM observation.

**References**

Study of Rare Gas Behaviour in Uranium Dioxide

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Pressurised Water Reactors (PWR)
- 80% of French electricity production
- Nuclear Fuel in PWRs
  - UO$_2$ pellets inside a tubular zirconium cladding

Generation of fission products (FP)
- 70% solid (Ru, Mo, Zr, Nd...)
- 30% gaseous (Xe, Kr) or volatile (Cs, I)
  → At 60 GWd/tM (5 annual cycles) : 0.5% at. Xe+Kr

Issue
- Fission Gas Releases (FGR) limit the fuel life time
- Fuel operating conditions are adjusted to maintain the FGR below a critical limit to keep the cladding integrity
STUDY GOALS AND EXPERIMENTAL PROCEDURE

To precisely model the fuel behaviour in-pile conditions
Necessity to understand the fuel physico-chemical properties

Experimental approach: Separate-effects studies
Non-active UO₂ - irradiation/implantation  Fine characterisation

Nucleation mechanisms
Transmission Electron Microscopy (TEM)
JANNUS Orsay Platform

Xenon Diffusion
Thermal Desorption Spectrometry (TDS)
PIAGARA Platform

2nd Int. MINOS Workshop - November 4-6, 2015, CEA – INSTN Cadarache, France
JANNuS platform in Orsay (France) Transmission Electronic Microscope coupled with a 2 MVolt accelerator (ARAMIS) and a 190 kVolt implanter (IRMA).

**in-situ** observation of the material microstructure modifications induced by ion irradiation/implantation.

- ARAMIS accelerator
- TEM
- IRMA implanter
- FEI Tecnai G2 200 kVolt
In situ study of Xe bubble nucleation coupling IRMA implantations and TEM

- Energy 390 keV
  - Majority of ions implanted in the thin foil
- Temperature at 600°C
- Fluence comprised between $3 \times 10^{12}$ and $7 \times 10^{14}$ ions.cm$^{-2}$
  - Atoms: $4 \times 10^{-4}$ to $10^{-1}$ at%
  - Defects: $2 \times 10^{-3}$ to 4 dpa

TEM

20 nm

6x$10^{12}$Xe.cm$^{-2}$
IN SITU STUDY OF XE BUBBLE NUCLEATION
IRMA IMPLANTATIONS AND TEM

Bubble Density (x10^{23} m^{-3})

Fluence (x10^{13} Xe cm^{-2})

bubble density increase up to a saturation of 4 \times 10^{23} m^{-3} for 2 \times 10^{14} ions cm^{-2}

Constant diameter 0.8 nm +/- 0.4 nm

A. Michel
NIMB 272 (2012)
IN SITU STUDY OF CAVITY NUCLEATION
ARAMIS IRRADIATION AND TEM

- Energy 4MeV
  - 98% of Au ions through the thin foil
  - creation only of defects
- Ambient temperature, 600°C and 1000°C
- Fluence comprised between $1.3 \times 10^{12}$ to $7 \times 10^{14}$ ions. cm$^{-2}$
  - Defects: $10^{-2}$ to 1.4 dpa
In situ study of cavity nucleation: Aramis irradiation and TEM

Variation of cavity density

Cavity density increases up to a saturation at $4.0 \times 10^{23}$ m$^{-3}$ for $10^{14}$ ions.cm$^{-2}$

Constant diameter 1.1 +/- 0.4 nm

Insoluble elements are not necessary to stabilize cavities until 1000°C

Heterogeneous nucleation on irradiation defects

C. Sabathier
NIMB 326 (2014)
STUDY OF XENON DIFFUSION IN UO$_2$
PIAGARA PLATFORM (CNRS/CENBG)

The platform is used to detect and analyse traces of isotopic rare gases with a detection limit of $10^5$ Kr or Xe atoms.

Effusion cell vacuum $10^{-8}$ Pa
T$<1400°C$

1. Extraction
2. Introduction
3. Calibration
4. Analysis

Mass spectrometer

Chemical traps

Balloon $^{131}$Xe

Mo crucible

Sample

Gas released

Ni

Magnet
- Implantation Xe at 400 keV
- Fluence $9 \times 10^{11}$ at.cm$^{-2}$ $\rightarrow$ 1.4 ppm $– 2.10^{-3}$ dpa
- Temperature range: 1150°C-1350°C

**SRIM simulation**

**Volume diffusion release**

**Burst release**

2nd Int. MINOS Workshop - November 4-6, 2015, CEA – INSTN Cadarache, France
**STUDY OF XENON DIFFUSION IN UO$_2$**

**PIAGARA PLATFORM (CNRS/CENBG)**

**MINOS**

- **Second Fick law**
  \[
  \frac{\partial C(x,t)}{\partial t} = \frac{1}{D(x)} \frac{\partial}{\partial x} \left( D(x) \frac{\partial C(x,t)}{\partial x} \right)
  \]

- **Limit conditions**
  \( C(0,t) = 0 \) and \( C(\infty,t) = 0 \)

- **Initial profile** \( C(x,0) \) : SRIM simulation

**Optimisation parameter:** \( D_s \) and \( D_v \)

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**Table: Xenon Diffusion Parameters**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( D(m^2.s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>1.8 ± 0.1.10$^{-22}$</td>
</tr>
<tr>
<td>1250</td>
<td>9.2 ± 0.5.10$^{-22}$</td>
</tr>
<tr>
<td>1300</td>
<td>9.9 ± 1.5.10$^{-22}$</td>
</tr>
<tr>
<td>1350</td>
<td>7.1 ± 0.6.10$^{-21}$</td>
</tr>
</tbody>
</table>

**Equation:**

\[
D_v(m^2.s^{-1}) = 6.3 \cdot 10^{-11} \exp\left(-\frac{3.3}{kT}\right)
\]
STUDY OF XENON DIFFUSION IN UO$_2$
PIAGARA PLATFORM (CNRS/CENBG)

- Important literature on xenon diffusion
  ⇒ dispersion on diffusion coefficient
- Experimental parameters to determine intrinsic diffusion coefficient
  ➢ burn-up
  ➢ stoichiometry

Using criteria on parameters
$BU<10^{22}$ fission.m$^3$
Stoichiometry controlled conditions
Selection of a few studies

Activation energy in agreement

$D_{\text{Xe}}^{\text{study}} < D_{\text{Xe}}^{\text{selection}}$

Kaimal’s study $10^{24}$ fission.m$^3$

In our study: low fluence to see nano cavity by TEM but xenon can be trapped in smaller irradiation defects
CONCLUSION AND PERSPECTIVE

- Study of the nucleation as a function of the ion fluence and temperature
  - No change in cavity size: diameter ~ 1 nm
  - Cavity density increases with fluence until a threshold density ~ $10^{23}$ cavity.m$^{-3}$
  - No dependence of temperature until 1000°C

  No need for insoluble elements to stabilize cavities until 1000°C
  Heterogeneous nucleation on irradiation defects

- Study of xenon diffusion
  - Determination of the Arrhenius law governing xenon diffusion
  - Although experiments are performed at very low implantation fluences, a trapped xenon effect can appear
  - Next experiments: xenon diffusion as a function of the fluence
    - Release measurements with PIAGARA Platform
    - Cavity characterisation by TEM
    - Defect characterisation by Positron Annihilation Spectroscopy (CEMHTI)