Study of Rare Gases Behavior in Uranium Dioxide

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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 UO₂ 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

Fig. 1: Plateform PIAGARA at CENBG laboratory

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.

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

References

- [1] A. Michel, C. Sabathier, G. Carlot, O. Kaïtasov, S. Bouffard, P. Garcia, C. Valot, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 272 (2012) 218.

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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

**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**

**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 3×10^{12} and $7 \times 10^{14} \text{ions.cm}^{-2}$
→ Atoms : 4×10^{-4} to $10^{-1} \text{at\%}$
→ Defects : 2×10^{-3} to 4 dpa

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

**Constant diameter
 $0.8 \text{ nm} \pm 0.4 \text{ nm}$**

**A. Michel
NIMB 272 (2012)**

- ❑ Energy 4MeV
 - 98% of Au ions through the thin foil
 - creation only of defects
- ❑ Ambient temperature, 600°C and 1000°C
- ❑ Fluence comprised between 1.3×10^{12} to 7×10^{14} ions. cm^{-2}
 - Defects : 10^{-2} to 1.4 dpa

**Insoluble elements are not necessary to stabilize cavities until 1000°C
Heterogeneous nucleation on irradiation defects**

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

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

SRIM simulation

Volume
diffusion
release

Burst release

- Second Fick law $\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D(x) \frac{\partial C(x,t)}{\partial x} \right)$
- 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

Temperature	$D(\text{m}^2.\text{s}^{-1})$
1150	$1.8 \pm 0.1.10^{-22}$
1250	$9.2 \pm 0.5.10^{-22}$
1300	$9.9 \pm 1.5.10^{-22}$
1350	$7.1 \pm 0.6.10^{-21}$

$$D_v(\text{m}^2.\text{s}^{-1}) = 6.3.10^{-11} \exp\left(-\frac{3.3}{kT}\right)$$

MINOS

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

Using criteria on parameters

$BU < 10^{22} \text{ fission.m}^{-3}$

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 $10^{24} \text{ fission.m}^{-3}$

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

□ 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 $\sim 10^{23}$ 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)