α Self-irradiation Effects on Structural Properties of (U,Am)O_{2±δ} Materials

Florent LEBRETON¹, Denis HORLAIT², Damien PRIEUR³, Philippe MARTIN¹,
Jean-Yves COLLE³, Arne JANSSEN³, Thierry WISS³, Andreas SCHEINOST⁴,
Thibaud DELAHAYE⁵

¹CEA-DEN-DTEC, Service d'Études des Combustibles et matériaux à base d'Actinides, SECA, (Marcoule, France)

²CEA-DEN-DTEC, Service de Développement des Technologies du Cycle, SDTC, (Marcoule, France)

³European Commission, Joint Research Centre, Institute for Transuranium Elements (Karlsruhe, Germany)

⁴Helmholtz Zentrum Dresden Rossendorf (HZDR), Institute of Resource Ecology (Dresden, Germany)

⁵CEA-DEN-DRCP, Service d'Étude du Recyclage des combustibles et d'Analyses, SERA, (Marcoule, France)

Am isotopes are amongst the largest contributors to the radiotoxicity and heat load of spent nuclear fuels, especially in scenarios including plutonium recycling in MOX fuels. Transmutation in heterogeneous mode is a promising option to lower Am inventory in the ultimate nuclear waste, thus decreasing the ecological impact of deep-geological repository sites. It consists in the irradiation Am-bearing blankets (AmBB, i.e., U_{1-x}Am_xO_{2±δ} with x values close to 10-15 at.%) in the periphery of a fast neutron reactor core. In this context, studies are being performed to assess the feasibility and safety of AmBB transmutation, notably focusing on innovative fabrication processes [1–3], AmBB behavior under irradiation [4] and U_{1-x}Am_xO_{2±δ} properties [5]. ²⁴¹Am being a strong α emitter (activity of 130 MBq), U_{1-x}Am_xO_{2±δ} behavior under α self-irradiation is also monitored [6–8].

One of the main effects of α radiation in crystallized materials is a structural swelling. U_{1-x}Am_xO_{2±δ} compounds with different Am/(U+Am) ratios (7.5 ≤ x ≤ 50 at.%) were monitored by X-ray diffraction (XRD) after a heat treatment during several months to observe their lattice parameter evolution with time. The results obtained first evidenced that the fluorite-type structure (*Fm-3m*) of the compounds remains stable all along the study. During the first days of storage, all samples underwent an oxidation, observed for the lowest Am/(U+Am) ratios (x ≤ 15 at.%) through a decrease of the lattice parameter or, for the other (30, 40 and 50 at.%), through an isostructural transition to a phase with a smaller lattice parameter (Fig. 1 left). After this phenomenon, an increase of the lattice parameter was observed for all the compositions, evidencing an asymptotic behavior leading to saturation after a few months. This evolution was fitted with the relation describing the structural swelling under α irradiation: $(a - a_0)/a_0 = A(1 - e^{-Bt})$, with a , the lattice parameter at a time t , a_0 the initial lattice parameter, A the relative swelling at saturation and, B , a kinetics constant. Satisfactory fitting results were obtained for all samples (with R²-factors superior to 99.5 %, see Fig 1 right). A parameters obtained indicate that all compositions present lattice swellings at saturation ranging from 0.26 to 0.28 %, with a small decrease with the Am content. The swelling kinetics logically increases with the Am content, but similar kinetics are obtained for all samples after normalization by the sample α activity. Additional experimental data was acquired using X-ray absorption spectroscopy (XAS), which confirmed the stability of the fluorite structure and that the different interatomic distances (actinide-O and actinide-actinide) present an evolution similar to that of the lattice parameter.

The effects of α self-irradiation in terms of structural disorder were also studied based on XRD and XAS data. Microstrain determined from XRD by the Williamson-Hall method did not exhibit any significant evolution with time (whereas it increases with the Am content, in line with previous results [5]). The Debye-Waller factors extracted from XAS however behaves similarly to the lattice parameter, i.e., increase followed by saturation, even though fewer points were available to give a precise trend. The reason for this discrepancy is probably that EXAFS gives information on the whole sample, including low-ordered or amorphous domains, whereas XRD results only concern crystallized domains. The Debye-Waller factor increase with time thus appears to be related to an accumulation of the α -induced defects in domains with no (or low) long range order, such as the vicinity of grain boundaries. This phenomenon of defect concentration then favors their recovery by recombination and is thus responsible for the saturation in both lattice parameter and defect increase with time.

Fig. 1: Evolution of $U_{1-x}Am_xO_2$ lattice parameters with time (left), and example of fit for the $U_{0.6}Am_{0.4}O_{2\pm\delta}$ compound (right).

Studies were also dedicated to the behavior of He atoms produced during α decay of ^{241}Am . A 5-year-old $U_{0.85}Am_{0.15}O_{2\pm\delta}$ sample was heat-treated up to 1500 K in a Knudsen cell coupled with a mass spectrometer (MS) allowing the quantification of released He. Transmission electron microscopy (TEM) observations were also performed on the sample before and after thermal treatment. Results show that a first He release occurs around 1000 K, followed by a main one around 1350 K, as shown in Fig. 2. The total quantity of He released during this heat treatment was estimated to represent about 75 % of the He produced by α disintegrations during the sample storage. TEM micrographs show that only subnanometric cavities (He bubbles) are observed before thermal treatment, whereas larger cavities are observed after, with diameters typically ranging between 2 and 5 nm. These results thus evidenced a coalescence of He trapped in the sample during the thermal treatment leading both to its release and to bubble growth.

Fig. 2: He release rate from a 5-year-old $U_{0.85}Am_{0.15}O_{2\pm\delta}$ sample measured by MS.

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F. Lebreton¹, D. Horlait², D. Prieur³, P. Martin¹,
J-Y. Colle³, A. Janssen³, T. Wiss³, A.
Scheinost⁴, T. Delahaye⁵

¹CEA-DEN-DTEC, Service d'Études des Combustibles et matériaux à base d'Actinides, SECA, (Marcoule, France)

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$U_{1-x}Am_xO_{2\pm\delta}$ compounds

- Americium is amongst the largest contributors to long-term radiotoxicity and heat load of ultimate nuclear waste from fuels
- To reduce this contribution: transmutation of Am in fast neutrons reactors
 - Am-doped MOX fuels
 - Inert-matrix-based targets
 - **Uranium-amerium mixed oxides: $U_{1-x}Am_xO_{2\pm\delta}$**
- Research ongoing regarding $(U,Am)O_2$ compounds
 - Fabrication processes
 - Behavior under irradiation
 - Structural and thermodynamic properties

$U_{1-x}Am_xO_{2\pm\delta}$ properties

- Fluorite-type structure^{1,2}
 - For Am/(U+Am) ratios from 0 to 70 at.%
- Peculiar cationic charge distribution^{1,3}
 - Americium behaving as a pure +III cation
 - Oxidation of U^{+IV} to U^{+V}
 - Charge compensation mechanism
 - Lattice parameters deviating from a UO_2 - AmO_2 Vegard law
- High α activity of ^{241}Am (1.3×10^{11} Bq.g⁻¹) led to studies on $U_{1-x}Am_xO_{2\pm\delta}$ behavior under self-irradiation
 - Storage before irradiation
 - Evaluation of the contribution of α -self-irradiation on other results

Measurements performed

- XRD monitoring of $U_{1-x}Am_xO_{2\pm\delta}$ (with different Am/(U+Am) ratios) evolution under self-irradiation for several months
 - Lattice parameter swelling with time
 - Influence of the Am content on the swelling
- Combined XAS/XRD characterization of $U_{1-x}Am_xO_{2\pm\delta}$ compounds with long storage time
 - Structural effects after long storage
 - Comparison between local and long-range structural effects
- Helium behavior in aged $U_{0.85}Am_{0.15}O_{2\pm\delta}$
 - Helium release during thermal annealing
 - TEM study before and after
 - Comparison between dense and “tailored-open-porosity” compounds

Sample preparation and XRD measurements

- $U_{1-x}Am_xO_{2\pm\delta}$ samples:
 - Prepared from UO_2 and AmO_2 powders employing the UMACS process¹
 - Final sintering for 4 hours at 2023 K under Ar- H_2 (+ O_2)
 - Various Am/(U+Am) ratios : from 7.5 to 70 at. %

- XRD monitoring:
 - Thermal treatment before measurements (1373 K, 1 h, Ar- H_2)
 - Anneal self-irradiation defects
 - Reduce O/M (oxygen to metal) ratio of the samples

 - Beginning of XRD measurements right after annealing
 - Sample ground to powder and mixed with gold (reference)
 - Measurements performed under ambient conditions
 - Acquisitions of 25-120°2 θ diffractograms in 30 min to 3 h

XRD MONITORING: INITIAL BEHAVIOR

Evolution of $U_{1-x}Am_xO_{2\pm\delta}$ compounds with time under air¹

■ Different behaviors during the first weeks of measurements:

■ 7.5 and **15** %Am

■ 30, **40** and 50 %Am

■ **60** and 70 %Am

- Oxidation of the samples (through a phase transition for $Am/(U+Am) \geq 30$ at.%)
- Single-phased compounds with the structure for all compositions after up to a few weeks
- Increase of lattice parameter

XRD MONITORING: LATTICE SWELLING

Evolution of $U_{1-x}Am_xO_{2\pm\delta}$ lattice parameters¹

- Similar evolutions for all compositions
 - Initial shrinkage (oxidation)
 - Lattice swelling then saturation:
 - Swelling kinetics increases with Am content
 - Similar kinetics as a function of the dose

$a(UO_2)$: 5.47 Å
 $a(AmO_2)$: 5.37 Å

Am/(U+Am) :

- 7.5 at.%
- 15 at.%
- 30 at.%
- 40 at.%
- 50 at.%
- 60 at.%
- 70 at.%

Evolution of $U_{1-x}Am_xO_{2\pm\delta}$ lattice parameters¹

■ Fitting lattice parameter evolution with time or α dose ($R^2 > 99\%$)²

■ Determination of three parameters:

- Initial lattice parameter: a_i
- Swelling at saturation: A
- Kinetics constant: B or B'

$$\frac{a_t - a_i}{a_i} = A(1 - e^{-B't})$$

$$= A(1 - e^{-BD\alpha})$$

Am/(U+Am) :

7.5 at.%

15 at.%

30 at.%

40 at.%

50 at.%

60 at.%

Evolution of $U_{1-x}Am_xO_{2\pm\delta}$ lattice parameters¹

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$$\frac{a_t - a_i}{a_i} = A(1 - e^{-B't})$$

$$= A(1 - e^{-BD\alpha})$$

- Variations with the Am content:

- Increase of swelling kinetics with the sample activity
- Small decrease of the swelling saturation for highest Am contents

Application of the Williamson-Hall method¹

■ No crystallite size variation observable ($L > 150$ nm)

■ Microstrain evolution

■ Increase with Am content

■ Slight increase for 7.5 at.%Am

Am/(U+Am) :

7.5 at.%

15 at.%

30 at.%

40 at.%

50 at.%

60 at.%

70 at.%

Measurements on aged samples

- $U_{1-x}Am_xO_{2\pm\delta}$ samples with Am ratios of 15 and 20 at.% aged for up to 1450 days studied using XRD and XAS

- Complementary to a previous study with samples aged for 20 and 200 days

- XAS measurements at Am L_{III} and U L_{II}/L_{III} edges

→ **XANES: Determination of cation oxidation states**

→ **EXAFS: Information on the local structure around each cation (Z, N, R, DW)**

- Both XANES and EXAFS are compared to reference compounds:

- U (L_{III}) edge:

- UO_2 (only **U^{+IV}**)
 - U_4O_9 (**U^{+IV}/U^{+V}** (50/50) and no **U^{+IV}**)¹
 - U_3O_8 (**U^{+V}/U^{+VI}** (66/33) and no **U^{+IV}**)¹

- Am (L_{III}) edge:

- AmO_2 (only **Am^{+IV}**)
 - (U,Am) mixed oxalate (only **Am^{+III}**)

Comparison of XANES spectra to references¹

- Am L_{III} edge
 - Sample spectra aligned with that of the reference for Am^{+III}
 - Am only present as Am^{+III}
- U L_{III} edge
 - Sample spectra between those of UO₂ and U₄O₉
 - Partial presence of U^{+V}
 - Fitting by linear combination
 - U^{+V} mole fraction close to that of Am^{+III}
- O/M ratios close to 2.00
- Behavior identical to that observed on “fresh” samples^{1,2}

EXAFS fitting using fluorite-type models¹

- Neither distortions nor coordination number changes → the structure remains fluorite-type
- Interatomic distances: no evolution after 220 days and up to 1400 days
- Structural disorder: no evolution of Debye-Waller factors after 220 days

Comparison between XRD and XAS results¹

- Lattice parameter (XRD) and interatomic distances (XAS)
 - Agreement of the two methods on an increase followed by a saturation
- Structural disorder: microstrain (XRD) and Debye-Waller factors (XAS)
 - No evolution of the microstrain with time²
 - Increase of the DW factors followed by a saturation

Comparison between XRD and XAS results¹

- Lattice parameter (XRD) and interatomic distances (XAS)
 - Agreement of the two methods on an increase followed by a saturation
- Structural disorder: microstrain (XRD) and Debye-Waller factors (XAS)
 - No evolution of the microstrain with time²
 - Increase of the DW factors followed by a saturation
- Comparison:
 - Agreement on fluorite-type structure conservation and a low disorder even after 4-year storages
 - Disagreement on the evolution of disorder with time
 - Long-range structure (XRD): no evolutions
 - Local structure (EXAFS): increase until saturation
 - **Accumulation of defects in low-ordered domains (GB proximity...)**
 - **Promotes defect recombination**
 - **Leads to saturation**

He BEHAVIOR: EXPERIMENTAL CONDITIONS

Study of helium behavior in $U_{1-x}Am_xO_{2\pm\delta}$

- Samples: $U_{0.85}Am_{0.15}O_{2\pm\delta}$ with two microstructures (MARIOS¹) stored for 4 to 5 years

- Dense
 - > 93 %TD
 - Open porosity < 2 %vol

- Tailored open porosity
 - < 87 %TD
 - Open porosity ≈ 10 %vol

- Measurements on helium release during thermal annealing
 - Performed in the ITU Knudsen cell (coupled with MS)
 - Helium released is analyzed using the Q-GAMES system²
- Characterization of samples before (and after) annealing
 - XRD/XAS
 - TEM

(U,Am)O_{2±δ} behavior under ²⁴¹Am-induced α self-irradiation

- Lattice swelling
 - Kinetic and saturation time depend on the sample activity
 - Saturation of about 0.8 vol% for all compositions
- Structural disorder
 - Low level of disorder even after 4-5 years of storage
 - Accumulation of defects in low-ordered domains → recombination and saturation
- He behavior
 - TEM reveals the presence of cavities and dislocation loops
 - He release rate up to 1500 K and increase of cavity size

- No detrimental consequences of self-irradiation for (U,Am)O₂ use as transmutation targets
- Helium diffusion starting around 900 K, lower than irradiation temperature

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