α Self-irradiation Effects on Structural Properties of (U,Am)O$_{2\pm\delta}$ Materials


$^1$CEA-DEN-DTEC, Service d’Études des Combustibles et matériaux à base d’Actinides, SECA, (Marcoule, France)
$^2$CEA-DEN-DTEC, Service de Développement des Technologies du Cycle, SDTC, (Marcoule, France)
$^3$European Commission, Joint Research Centre, Institute for Transuranium Elements (Karlsruhe, Germany)
$^4$Helmholtz Zentrum Dresden Rossendorf (HZDR), Institute of Resource Ecology (Dresden, Germany)
$^5$CEA-DEN-DRCP, Service d’Étude du Recyclage des combustibles et d’Analyses, SERA, (Marcoule, France)
CONTEXT: AMERICIUM TRANSMUTATION

$U_{1-x}Am_xO_{2\pm\delta}$ 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-americium 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
**CONTEXT: AMERICIUM TRANSMUTATION**

**U_{1-x}Am_xO_{2±δ} 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\(_x\)O\(_{2±δ}\) behavior under self-irradiation
  - Storage before irradiation
  - Evaluation of the contribution of α-self-irradiation on other results

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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

- $U_{1-x}Am_xO_{2+δ}$ samples:
  - Prepared from $UO_2$ and $AmO_2$ powders employing the UMACS process\(^1\)
  - 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°$2θ$ diffractograms in 30 min to 3 h

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XRD MONITORING: INITIAL BEHAVIOR

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

- 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 $U_{1-x}Am_xO_{2±δ}$ lattice parameters

- 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

$$a(UO_2): \quad 5.47 \text{ Å}$$
$$a(\text{AmO}_2): \quad 5.37 \text{ Å}$$

Am/(U+Am) :
- 7.5 at.%
- 15 at.%
- 30 at.%
- 40 at.%
- 50 at.%
- 60 at.%
- 70 at.%

XRD MONITORING: FITTING LATTICE SWELLING

Evolution of $U_{1-x}Am_xO_{2\pm\delta}$ lattice parameters\(^1\)

- Fitting lattice parameter evolution with time or $\alpha$ dose ($R^2 > 99\%$)\(^2\)
  - Determination of three parameters:
    - Initial lattice parameter: $a_i$
    - Swelling at saturation: $A$
    - Kinetics constant: $B$ or $B'$

\[
\frac{a_t - a_i}{a_i} = A(1 - e^{-B't}) = A(1 - e^{-BD\alpha})
\]

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Am/(U+Am): 
- 7.5 at.%
- 15 at.%
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- 40 at.%
- 50 at.%
- 60 at.%

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

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

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

\[
\frac{a_t - a_i}{a_i} = A(1 - e^{-B't}) = A(1 - e^{-B^\prime D\alpha})
\]

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XRD MONITORING: MICROSTRAIN AND CRYSTALLITE SIZE

Application of the Williamson-Hall method\(^1\)

- No crystallite size variation observable (L > 150 nm)
- Microstrain evolution
  - Increase with Am content
  - Slight increase for 7.5 at.\% Am

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- 50 at.\%
- 60 at.\%
- 70 at.\%

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Measurements on aged samples

- $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\delta}$ 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 $L_{\text{III}}$ and U $L_{\text{II}}/L_{\text{III}}$ 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 ($L_{\text{III}}$) edge:
  - $\text{UO}_2$ (only $\text{U}^{+\text{IV}}$)
  - $\text{U}_4\text{O}_9$ ($\text{U}^{+\text{IV}}/\text{U}^{+\text{V}}$ (50/50) and no $\text{U}^{+\text{IV}}$)
  - $\text{U}_3\text{O}_8$ ($\text{U}^{+\text{V}}/\text{U}^{+\text{VI}}$ (66/33) and no $\text{U}^{+\text{IV}}$)

- Am ($L_{\text{III}}$) edge:
  - $\text{AmO}_2$ (only $\text{Am}^{+\text{IV}}$)
  - (U,Am) mixed oxalate (only $\text{Am}^{+\text{III}}$)

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Comparison of XANES spectra to references\textsuperscript{1}

- Am L\textsubscript{III} edge
  - Sample spectra aligned with that of the reference for Am\textsuperscript{+III}
  - Am only present as Am\textsuperscript{+III}

- U L\textsubscript{III} edge
  - Sample spectra between those of UO\textsubscript{2} and U\textsubscript{4}O\textsubscript{9}
  - Partial presence of U\textsuperscript{+V}
  - Fitting by linear combination
  - U\textsuperscript{+V} mole fraction close to that of Am \textsuperscript{+III}

  \(\triangleright\) O/M ratios close to 2.00

- Behavior identical to that observed on “fresh” samples\textsuperscript{1,2}

EXAFS fitting using fluorite-type models\textsuperscript{1}

- Neither distortions nor coordination number changes $\rightarrow$ 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 results

- 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 time
  - Increase of the DW factors followed by a saturation

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  - No evolution of the microstrain with time
  - 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
Study of helium behavior in $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\delta}$

- Samples: $\text{U}_{0.85}\text{Am}_{0.15}\text{O}_{2\pm\delta}$ with two microstructures (MARIOS$^1$) stored for 4 to 5 years
  - Dense
    - $> 93\%$TD
    - Open porosity
      - $< 2\%$vol
  - Tailored open porosity
    - $< 87\%$TD
    - Open porosity
      - $\approx 10\%$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 system$^2$

- Characterization of samples before (and after) annealing
  - XRD/XAS
  - TEM

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CONCLUSIONS

(U,Am)O$_{2±δ}$ behavior under $^{241}$Am-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 $\rightarrow$ 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)O$_2$ use as transmutation targets
- Helium diffusion starting around 900 K, lower than irradiation temperature
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References