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Structure of mixed U(IV)–An(III) precursors synthesized by co-conversion methods (where An = Pu, Am or Cm)

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ABSTRACT

Current concepts for future nuclear systems aim at improving the fuel cycle with the main following criteria: economy of resources, minimized volume and lower long-term potential radiotoxicity of ultimate wastes and proliferation risk reduction. Co-management of two (or more) actinides has recently been proposed for recycling reusable energy-producing actinides (mainly U and Pu) together, or for transmuting radiotoxic minor actinides within UO_2-based materials. Co-conversion processes play an important role by closing the actinide separation–purification operations and at the same time producing mixed actinide solid compounds for the fabrication of fresh fuel. Handling of actinides mixtures, from the initial solution up to the solid product, requires innovative synthesis methods and structures, particularly for the minor actinides such as americium and curium. Considering the different designs of future nuclear fuels, various uranium–actinide co-conversion routes are currently investigated in the CEA-ATALANTE facility.

1. Introduction

One major fuel cycle option currently under evaluation for Generation III/IV systems is co-management of the actinides (An) in an integrated closed fuel cycle [1]. The main objectives are efficient use of the energy-producing resources by recycling the major actinides such as uranium and plutonium, and a drastic decrease in the radiotoxicity of the ultimate wastes by partitioning and transmuting the minor actinides such as americium, curium or neptunium. Co-management implies separating these actinides from the fission products, most often by hydrometallurgical processes, and then converting them to solid forms to refabricate fresh fuel or dedicated fuels or targets. It also implies that these materials are polymetallic, containing major and/or minor actinides. The involvement of significant amount of minor actinides (MAs) and the need for more complex compositions and multi-scale structures have led to renewed interest in wet synthesis routes [2]. Considering the different designs of future nuclear fuels, including mixed actinide pellets, composite materials or spherical particles, various uranium–actinide co-conversion routes are currently being investigated in the CEA-ATALANTE facility, particularly the oxalic process (*via* a coprecipitation step).

Our first challenge is to control the immobilization of the actinides into a solid compound from a mixture of actinides in solution typically at the end of the partitioning steps. As this mixed solid compound would be the solid precursor of a material such as a new fuel or a dedicated target, controlling its composition homogeneity at molecular scale and its physicochemical properties could be of major importance [3].

The main experiments described were recently performed by the CEA at Marcoule, in the ATALANTE facility.

2. Experimental

2.1. Reagents

Uranium(IV), plutonium(III), americium and curium stock solutions were prepared either from purified monometallic solutions or by dissolving monometallic oxides or hydroxides. Hydrazinium nitrate ($N_2H_5^+, NO_3^-$) was used as an anti-nitrous agent to stabilize the lowest oxidation states (typically +IV for U and +III for Pu). The concentration, purity and oxidation state were determined by UV–visible spectroscopy.

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2.2. Synthesis methods

Various approaches are used in ATALANTE: oxalate coprecipitation, sol-gel (internal gelation or colloidal), resin impregnation, etc. The first approach, the subject of this paper, takes advantage of the ability of the oxalate ligand to form insoluble complexes with An(IV) and An(III) in acidic solution [4]; under optimized conditions, this can result in novel mixed crystallographic structures with unprecedented characteristics at a molecular scale. Various microstructures can be obtained by varying chemical parameters (acidity, oxalic acid excess) during the coprecipitation step in a vortex effect reactor.

All synthesized U(IV)–An(III) mixed oxalate compounds (where An = Pu, Am or Cm) were calcined into oxide at 900 °C in flowing argon.

2.3. XRD acquisition

XRD data were acquired using a Bruker D8-advance diffractometer with a molybdenum anticathode. The sample was placed under Mylar film to prevent material removal and was placed in a leak-tight container with a Be window specifically designed by the CEA. Gold was added to all the samples as an internal standard to calibrate the angular positions of the observed XRD lines. Cellulose was used as a diluting agent to reduce the quantity of radioactive sample and then the dose rate. The lattice parameters of the mixed oxalates and oxides were refined by pattern matching using FullProf [5].

2.4. Scanning electron microscope data acquisition and analysis

Two scanning electron microscopes (SEM) available in ATALANTE were used: (1) a JEOL T 330A, installed in a hot cell (8 cm steel) for highly radioactive samples, allows secondary electron imaging; (2) a JEOL JSM 5600LV, used for uranium and/or non-radioactive sample analysis, allows secondary and backscattered electron imaging. In both the cases, samples were deposited on a carbon substrate bonded to the sample holder, and then metallized with gold for 4 min.

2.5. EXAFS data acquisition and analysis

All XAS measurements were performed at the European Synchrotron Radiation Facility (Grenoble, France) at the BM20 beam line. Teflon sample holders were attached to the cold finger of a He cryostat, so the sample temperatures were near 15 K. For each sample, uranium L_{III}-edge (17166 eV) and plutonium L_{II}-edge (22266 eV) spectra were collected. All plutonium spectra were recorded in fluorescence mode using a 13-element Ge detector. Dead time correction ensured that the absorption peak height matched the transmission data. Uranium XAFS spectra were recorded in transmission mode. Energy calibrations were accomplished using Y foil (17038 eV) or Mo foil (20000 eV) positioned after the second ionization chamber. ATHENA software [6] was used to extract EXAFS oscillations from the raw absorption spectra. Experimental EXAFS spectra were Fourier transformed using a Kaiser-Bessel window ($dk = 2.5$) over a k space range of 2.1–13.8 Å^{-1} for both plutonium and uranium. Curve fitting was performed in k^3 for R values in the range of 1.5–4.3 Å using FEFF8.20 [7] calculations at both edges.

3. Results and discussion

Depending on the chemical conditions, the oxalate coprecipitate is constituted either by a mix of monometallic oxalates or, more advantageously considering the above-mentioned criteria for the future nuclear fuel cycles, by a single-phase polymetallic oxalate. Under suitable conditions, the oxalate ligand can coordinate a tetravalent actinide and a trivalent one in an original way in the solid. For U(IV)–An(III) mixtures (An = Pu, Am), a new recently described [8,9] mixed hexagonal structure was obtained. The originality of this structure is based on a mixed crystallographic site that can accept either a tetravalent or a trivalent actinide, the charge balance being ensured by adjustment of the single-charged ions within the structure in the second coordination shell.

The major contribution of this work is an extended investigation of the formation domain of this particular structure by coprecipitating U(IV) and Cm(III) (90/10) in a specific shielded cell of the ATALANTE facility. We found that the U(IV)/Cm(III) (90/10) oxalate crystallizes in the same hexagonal system as U(IV)/Pu(III) or U(IV)/Am(III) does (Fig. 1). The U(IV)–An(III) crystallographic mixed site in this oxalate hexagonal structure is responsible for the homogeneous distribution of actinides in the coprecipitates. Moreover, we established that solid solution domains exist over a wide range of U(IV)/Nd(III) ratios (from 100/0 up to 50/50) for this same structure (Nd used as An(III) surrogate) [8]. This interesting feature can thus also be obtained for the U(IV)/An(III) systems with the trivalent actinide varying from plutonium up to curium (probably with different existence domains due to the decrease in the An(III) ionic radii along the actinide series).

Metallic oxalate salts are well-known precursors of oxide phases. The mixed U(IV)–An(III) oxalates are very interesting

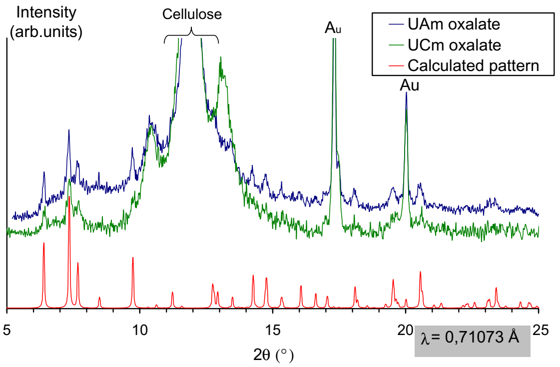

Fig. 1. X-ray diffraction patterns of the mixed U–Am (90/10) and U–Cm (90/10) oxalates synthesized by oxalic U(IV)–An(III) coprecipitation (crystallized in the previously described hexagonal system).

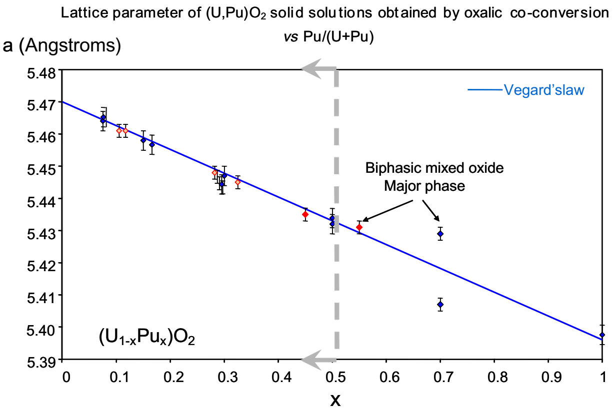

Fig. 2. Evolution of the lattice parameter a with Pu content in $(U,Pu)O_2$ solid solution, measured by XRD and compared with Vegard's law.

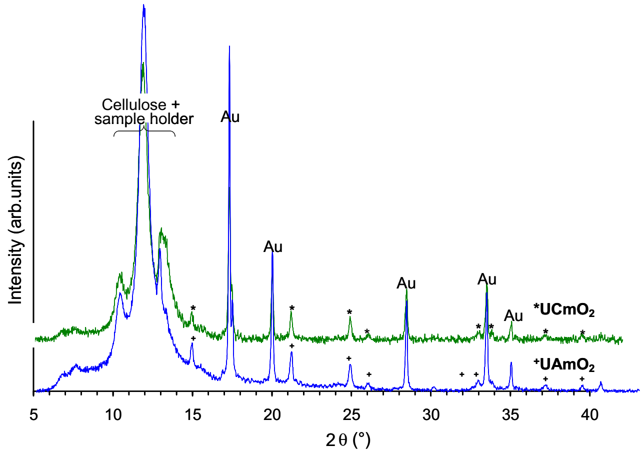

Fig. 3. X-ray diffraction patterns of the mixed uranium–americium (90/10) and uranium–curium (90/10) oxides synthesized by oxalic U(IV)–An(III) co-conversion.

mixed oxide precursors. After suitable heat treatment, oxide solid solutions are indeed formed, as demonstrated by the relationship between the lattice parameter of the face-centered cubic oxide and the Pu/U ratio in Fig. 2. The composition homogeneity at sub-micron scale is then maintained by ensuring suitable conditions during both coprecipitation and heat treatment.

Moreover, the diffraction patterns of the mixed uranium–americium (90/10) and uranium–curium (90/10) oxides are also characteristic of the face-centered cubic $(U,Am)O_2$ and $(U,Cm)O_2$ solid solutions (Fig. 3). The calculated lattice parameters, $a = 5.445(3)$ Å and $a = 5.449(1)$ Å, respectively, are slightly lower than the values expected from Vegard's law. This indicates that the oxygen/metal ratio is probably less than 2.00, the minor actinide being mainly at the fourth oxidation state, but partially at the third oxidation state due to the partial reduction of these minor actinides at relatively high temperatures, as often observed for the single oxide of these elements [10,11].

This result highlights the high homogeneity of the distribution of the studied minor actinides in the $(U,AM)O_2$ mixed oxide, probably at molecular scale. This feature is highly important when handling this type of material, because it prevents the dissemination of very contaminated dust composed only of AmO_{2-x} or CmO_{2-x}. It can even diminish the dose rates thanks to the shielding of uranium or minimize partial volatilization of Am and Cm at high temperatures during sintering, contrary to what may be observed when processing single oxides of these minor actinides.

SEM examination (Fig. 4(a) and (b)) revealed that the morphology of the co-converted U–Cm mixed oxide is quite similar to the corresponding U(IV)–Cm(III) oxalate precursor, even if the average particle diameter was smaller by about a factor of 2 due to the mass loss. By varying the coprecipitation conditions, it should then be possible to modify the morphology of the oxalate and then the oxide particles and to optimize the powder characteristics for subsequent fuel fabrication. For example, under more acidic coprecipitation conditions, significantly different morphologies (Fig. 4(c) and (d)) were obtained for the U(IV)–Nd(III) oxalate coprecipitate (which crystallizes in the same hexagonal system as the (U(IV)–Cm(III) one).

A more thorough structural investigation was carried out by EXAFS to better characterize at a molecular scale the mixed oxides synthesized with a Pu/(U+Pu) ratio not exceeding 50 % by the described oxalic method. The changes in the uranium and plutonium local environment are summarized in Fig. 5. For both actinides, the overall shape of the spectra is the same with two main peaks located near 2 Å (corresponding to the first An–O coordination shell) and 4 Å (corresponding to the An–An shell and second An–O shell). The same environment is observed in the UO_2 reference sample (the difference in the intensity is due to the fact that this spectrum was collected at room temperature), and thus corresponds to a face-centered cubic structure. EXAFS fits confirmed this observation; as for all compositions the same environment is obtained

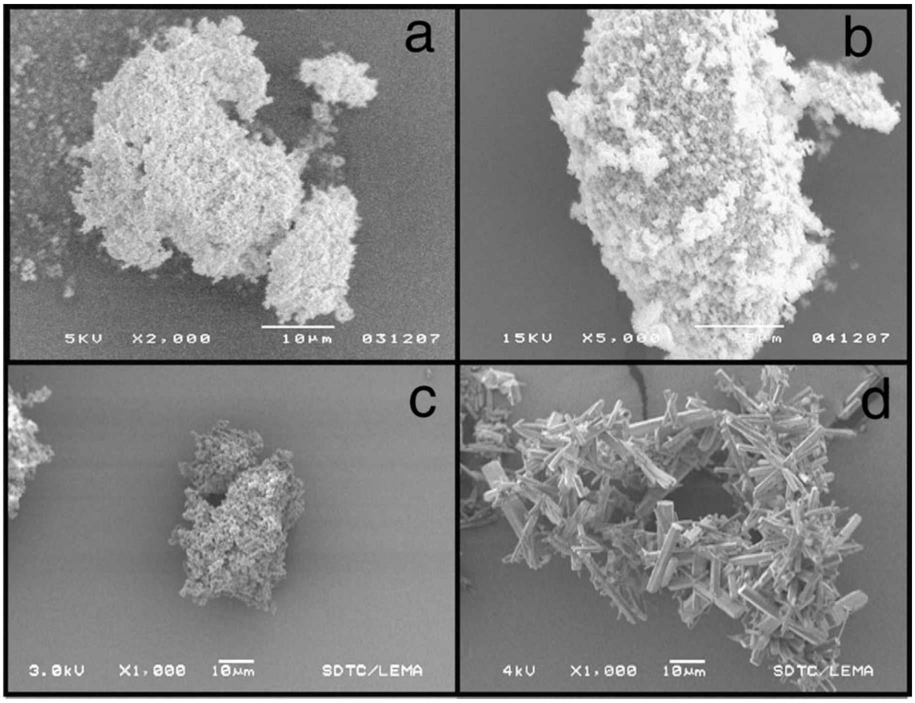

Fig. 4. Comparison of the morphology obtained by SEM of U–An powders: a mixed U–Cm oxalate (a); the corresponding mixed U–Cm oxide (b) after calcination; mixed U–Nd oxalates synthesized under different coprecipitation conditions (HNO_3 = 1 mol/L (c) vs. HNO_3 = 2.5 mol/L (d)).

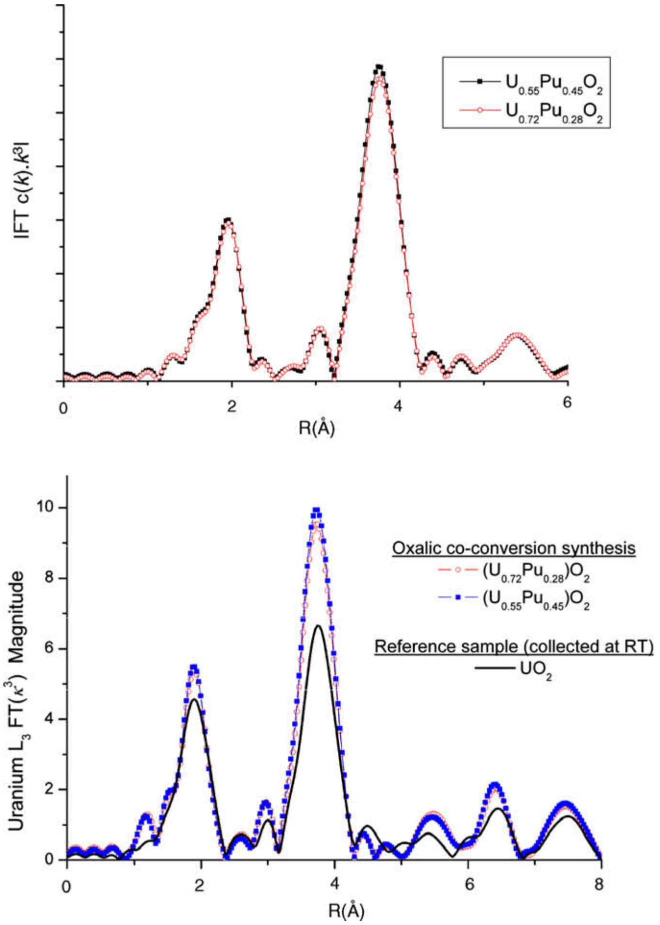

Fig. 5. Fourier transforms of plutonium L_{II}-edge and of uranium L_{III}-edge EXAFS spectra of (U,Pu)O_2 solid solutions synthesized by oxalic co-conversion.

for both the cations (limit values given correspond to $U_{0.55}Pu_{0.45}O_2$ and $U_{0.85}Pu_{0.15}O_2$ samples): a first coordination shell of eight oxygen atoms at distances ranging from 2.34 to 2.35 Å, and a second coordination shell including 12 U+Pu atoms at distances varying between 3.84 and 3.86 Å. Moreover, a shortening of bond lengths is evidenced as the plutonium concentration increases. Unlike previous results [12], no disordered hyperstoichiometric structure $(U_{1-y}Pu_y)O_{2+x}$ has been observed for samples with a plutonium content below 50 at.%. These results clearly demonstrate the formation of an ideal (U,Pu)O_2 solid solution using this oxalic co-conversion method *via* the coprecipitation of a U(IV)–Pu(III) mixed oxalate.

Similar investigations are very difficult to carry out with uranium–curium oxides due to the high neutron emission of common available isotopes, but are planned in the near future with mixed uranium–americium oxides.

4. Conclusion

The initial experimental developments of the U(IV)–Am(III) or U(IV)–Cm(III) oxalic co-conversion method, coupled with structural investigations, highlight some common interesting structural features of the solid products at either the oxalate or the oxide step with reference to the more thoroughly investigated U(IV)–Pu(III) process. Intermediate between the separation and the fabrication of transmutation targets or blankets, the oxalic co-conversion to oxide extended to minor actinides could be used in advanced fuel cycles to produce very homogeneous mixed oxides with particle microstructures that can be modulated at the coprecipitation step from the U(IV)–An(III) oxalate precursor. This dilution homogeneity within the UO_2 matrix is an interesting characteristic considering the high radioactivity and thermal emission of americium and especially of curium. Moreover, it could be achieved by using reagents and process equipment already proven for plutonium conversion by more than 50 years of experience at industrial scale.

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References

[1] US DOE Nuclear Research and Advisory Committee and the Generation IV International Forum, A Technology Roadmap for Generation IV Nuclear Energy Systems, December 2002.
[2] S. Pillon, J. Somers, S. Grandjean, J. Lacquement, J. Nucl. Mater. 320 (2003) 36.
[3] S. Grandjean, B. Chapelet-Arab, S. Lemonnier, A.-C. Robisson, N. Vigier, Innovative synthesis methods of mixed actinides compounds: control of the composition homogeneity at a molecular or nanometric scale, in: MRS Symposium Proceedings of Materials Research Society, vol. 893, 2006.
[4] S. Grandjean, A. Beres, J. Rousselle, C. Maillard, World Patent WO 2005/119699, 2005.
[5] J. Rodriguez Carjaval, M.T. Fernandez Diaz, J.L. Martinez, J. Phys. Condens. Matter 3 (1991) 3215.
[6] B. Ravel, M. Newville, J. Synchrotron Rad. 12 (2005) 537.
[7] J.J. Rehr, R.C. Albers, Rev. Mod. Phys. 72 (2000) 621.
[8] B. Arab-Chapelet, S. Grandjean, G. Nowogrocki, F. Abraham, J. Nucl. Mater. 373 (2008) 259.
[9] B. Arab-Chapelet, S. Grandjean, G. Nowogrocki, F. Abraham, J. Alloy. Compound. 444&445 (2007) 387.
[10] R.J.M. Konings, J. Nucl. Mater. 298 (2001) 255.
[11] C. Thiriet, R.J.M. Konings, J. Nucl. Mater. 320 (2003) 292.
[12] P. Martin, S. Grandjean, C. Valot, G. Carlot, M. Ripert, P. Blanc, C. Hennig, J. Alloy. Compound. 444&445 (2007) 410.