Journal of Nuclear Materials 483 (2017) 158–166

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Long-term behavior of refractory thorium-plutonium dioxide solid solutions

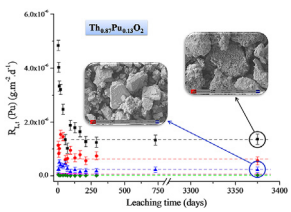
Laurent Claparede [a, *], Mireille Guigue [b], Gauthier Jouan [c], Nassima Nadah [b], Nicolas Dacheux [a], Philippe Moisy [b]

[a] ICSM, UMR 5257 CNRS/CEA/Univ. Montpellier/ENSCM, Site de Marcoule, Bât. 426, BP 17171, 30207 Bagnols/Cèze, France
[b] CEA, Nuclear Energy Division, RadioChemistry & Processes Department, BP 17171, 30207 Bagnols/Cèze, France
[c] CEA, Nuclear Energy Division, DTEC Department, BP 17171, 30207 Bagnols/Cèze, France

HIGHLIGHTS

- Leaching tests of $Th_{0.87}Pu_{0.13}O_2$ were performed for 9 years in several nitric acid solutions.
- The high chemical durability of thorium-plutonium oxide solid solutions was confirmed.
- The solubility of plutonium(IV) was not controlled by the precipitation of plutonium tetrahydroxide in these experiments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2016
Received in revised form
2 November 2016
Accepted 4 November 2016
Available online 5 November 2016

Keywords:
Thorium
Plutonium
Oxide
Dissolution
Leaching
Long-term storage

ABSTRACT

The long-term behavior of $Th_{0.87}Pu_{0.13}O_2$ was examined in nitric acid concentrations. The normalized dissolution rates after 3380 days, range from $(1.4 \pm 0.2) \times 10^{-6}$ g m^{-2} d^{-1} in 5 M HNO_3 down to $(3.2 \pm 0.4) \times 10^{-8}$ g m^{-2} d^{-1} in 10^{-3} M HNO_3, which confirms the high chemical durability of this solid solution. The amounts of plutonium measured in solution lead to 0.9% and 2.1% of dissolved solid in 1 M and 5 M HNO_3, respectively. In such conditions, the time required to reach the full dissolution of the material varies from 430 years (5 M HNO_3) to 18,000 years (10^{-3} M HNO_3). Moreover, the partial order related to the proton activity ($n = 0.45 \pm 0.03$) suggests that the dissolution is mainly driven by surface reactions occurring at the solid/liquid interface. The characterization of the leached samples by SEM shows small microstructural modifications (i.e. detachment of crystallites) and the absence of neoformed phase while from PXRD, the unit cell parameter and crystallite size are not significantly affected.
© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Mixed actinide dioxides are currently used as fuels in Pressurized Water Reactors (PWR) (including Gen III, EPR) and also stand as potential candidates for several Gen IV concepts including Sodium-cooled Fast Reactor (SFR) or Gas-cooled Fast Reactor (GFR) [1,2]. Moreover, the reprocessing of minor actinides coming from spent nuclear fuel into mixed-oxide fuels or in UO_2-based blankets surrounding the core is also often considered [3]. On the other hand, thoria (ThO_2) presents a great interest for its potential use in the field of several nuclear energy applications. Although ^{232}Th does not correspond to a fissile isotope, it can produce ^{233}Th ($T_{1/2} = 21.8$ min) by neutron capture then ^{233}Pa ($T_{1/2} = 27$ d) and finally ^{233}U (fissile isotope, $T_{1/2} = 1.6 \times 10^4$ yr) by two successive β^-

* Corresponding author. Laboratory of Evolving Interfaces in Materials, ICSM/LIME – UMR 5257, Site de Marcoule, Bât 426, BP 17171, 30207 Bagnols sur Cèze, France.
E-mail address: laurent.claparede@umontpellier.fr (L. Claparede).

http://dx.doi.org/10.1016/j.jnucmat.2016.11.007
0022-3115/© 2016 Elsevier B.V. All rights reserved.

decays. With the renewal of nuclear power, the thorium nuclear fuel cycle also received an increased interest because of several physico-chemical properties (high fusion temperature, rather simple thermodynamic diagram compared to uranium, good sintering capability and resistance to radiation damage, reduction of the transuranium elements production compared to uranium …) and its greater natural abundance [4]. The potentiality of the thorium resources has been often recognized, especially in several countries with large thorium reserves such as India [5]. Additionally, thoria-based fuels also provide an attractive option for the transmutation of minor actinides [6] or to burn the excess military weapon grade plutonium coming from the disposition programs [4].

Moreover, thorium-based dioxides are usually associated with very high performances in the field of the direct disposal for long-term storage (very high resistance to aqueous alteration or corrosion). This property is mainly associated to very low normalized dissolution rates and to the rapid establishment of saturation processes [7,8]. While the multiparametric study of the $Th_{1-x}U_xO_2$ dissolution was already examined by varying several conventional parameters such as temperature, chemical composition or leachate acidity [7,9–11], that of $Th_{1-x}Ce_xO_2$ [12] and $Th_{1-x}Pu_xO_2$ [13] remained poorly examined.

Other studies were dedicated to the optimization of the operating conditions for the dissolution of PuO_2 [14–16]. Even if the conclusions on the mechanisms involved were far less numerous for PuO_2, they all demonstrated the strong refractory nature of this material in oxidative conditions [17,18]. Such property was also underlined for CeO_2 which was generally reported to be strongly resistant to corrosion in nitric acid media even if nitrogen species played a significant role as promoting reagent for ceria dissolution [19,20].

In this paper, we describe dissolution experiments extended up to 9 years in several nitric acid concentrations on highly refractory $Th_{0.87}Pu_{0.13}O_2$ solid solutions in order to verify whether the initial kinetics is conserved and to identify additional potential mechanisms that could affect the plutonium releases when extending the leaching time.

2. Experimental

2.1. Preparation of thorium - plutonium dioxide solid solutions

Tetravalent actinides were simultaneously precipitated by addition of an excess of ammonium oxalate solution (0.2 M) in 3.5 M HNO_3. The precipitate was washed several times with deionized water, filtered, dried, and then finally heated in air in a glovebox, using a tubular furnace at 900 °C for 12 h after a preheating step at 100 °C for 1 h. The stoichiometry of the sample was verified after the complete dissolution of the solids in 14 M HNO_3/ 5×10^{-2} M HF by determination of the concentration of both actinides using ICP-MS. The specific activity of plutonium used for this synthesis reached 3.62×10^9 Bq/g Pu. The isotopic composition of the plutonium used in the synthesis is described in Table 1. The two main plutonium isotopes (>99.5%) corresponded to ^{239}Pu ($T_{1/2} = 2.4 \times 10^4$ yrs, α emitter) and ^{240}Pu ($T_{1/2} = 6.5 \times 10^3$ yrs, α emitter) that minimized the creation of defects in the solid due to alpha radiolysis. Indeed, the isotopic ratio of ^{241}Pu ($T_{1/2} = 14.4$ yrs, β emitter) and ^{238}Pu ($T_{1/2} = 87.7$ yrs, α emitter) only reached 0.03% and 1.8 10^{-3}%, respectively.

Table 1
Isotopic composition of Pu.

Isotope	$t_{1/2}$ (years)	%
^{239}Pu	24 111	97.09
^{240}Pu	6 563	2.87
^{241}Pu	14.35	0.03
^{242}Pu	375 000	0.0084
^{238}Pu	87.7	0.0018

2.2. Characterization

All the samples prepared were characterized through XRD and EXAFS before leaching tests, as already described in a previous paper [21]. The specific surface area of each sample was measured by the Brunauer-Emmett-Teller (BET) method, using 10-point N_2 - adsorption isotherms on a COULTER SA 3100 apparatus. The sample degassing lasted 10 h at 100 °C prior the determination of the specific surface area. The values obtained for $Th_{0.87}Pu_{0.13}O_2$ solid solutions were found to be 4.9 ± 0.1 m^2 g^{-1}.

2.2.1. Powder X-Ray diffraction

For PXRD analyses, about 10–30 mg of each sample (leached or annealed at 900 °C for 12 h) were ground in an agate mortar and mixed with 10–20 mg of gold powder as internal reference. PXRD patterns were recorded at room temperature in the 2θ range 10–120° with steps of 0.01° and counting time of 1 s per step, using a Bruker D8 Advance with a Cu Kα sealed tube ($K\alpha_1/\alpha_2$, λ = 1.54,249 Å) and LynxEye linear fast detector. LaB_6 standard NIST powder was used for the calibration of the apparatus. To perform those measurements, a nuclearized sample holder with a beryllium X-ray transparent window was used.

2.2.2. SEM

Scanning electron microscopy (SEM) observations in secondary electron mode with Everhart-Thornlay detector (SE2) or Inlens detector have been performed with a Zeiss SUPRA 55 WDS nuclearized apparatus in Atalante facility (CEA of Marcoule). Micrographs were recorded at different magnifications, working distances and acceleration voltage. Preparation of leached and unleached samples was done by sprinkling powders on carbon adhesives disks and covering each sample holder with a thin layer of gold performed by PVD with Polaron SC7640 apparatus during 3 min.

2.3. Leaching experiments

The first leaching experiments were initiated in 2002. The long-term dissolution experiments were carried out in batch reactors. Pretreated powdered samples (100 mg) were placed in acid-cleaned Nalgene bottles (high-density polyethylene) with 10 mL of solution. The S/V ratios considered for these experiments were equal to 500 cm^{-1} for $Th_{0.87}Pu_{0.13}O_2$. After settling, an aliquot of 100 μL of the leachate was taken off then renewed with fresh solution at regular intervals to determine the evolution of the elementary releases during 280 days. In such conditions, less than 1% of the leachate was removed in order to avoid any perturbation in the establishment of saturation processes at the solid/liquid interface. Aliquots were then centrifuged at 13,000 rpm to avoid the presence of colloids smaller than 11 nm [22]. The elementary plutonium concentrations were determined by α-liquid scintillation technique (PERALS ™). KNO_3/HNO_3 mixtures were considered in order to maintain an ionic strength (I) to 0.1 M.

9 years later (i.e. in 2011), the solids were fully separated from the solutions then the altered samples of $Th_{0.87}Pu_{0.13}O_2$ were characterized by SEM and PXRD. The leached solids were thus contacted again during 2 years with fresh 5 mL of solution (10^{-1} M and 5 M HNO_3) to study the impact of a second dissolution step on the chemical durability of the materials. A third dissolution step

Download English Version:

https://daneshyari.com/en/article/5454297

Download Persian Version:

https://daneshyari.com/article/5454297

Daneshyari.com