Progress in Nuclear Energy 72 (2014) 91–95

Contents lists available at ScienceDirect

Progress in Nuclear Energy

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

X-ray absorption in plutonium uranium mixed oxide fuel: Thorium characterization

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ARTICLE INFO

Article history:
Received 2 September 2013
Received in revised form
6 September 2013
Accepted 11 September 2013

Keywords:
Thorium
Mixed oxide
Fuel
X-ray absorption spectroscopy

ABSTRACT

Plutonium uranium mixed oxide (MOX) fuels are currently used in nuclear light water reactors. Thorium can be found in pristine as well as irradiated MOX samples. In normal conditions this element is only present in one oxidation state (IV), therefore its characterization can be used as a solid base for later studies of other actinides with the same oxidation state.

In this work, the atomic structure and nearest-neighbor environment of thorium within pristine and irradiated MOX samples were analyzed by micro-X-ray absorption fine structure (μ-XAFS) spectroscopy measured in fluorescence mode. To serve as a reference, spectra of pure thoria (ThO_2) powder samples were recorded. It was found that thorium is only present in its most common state (tetravalent) in both pristine and irradiated fuels. The structure of the thorium dioxide and MOX samples was modeled and their respective spectra were calculated. This modeling is consistent with the experimental conclusions.

1. Introduction

Uranium- plutonium mixed oxide (MOX) $(U,Pu)O_2$ fuels have been used in light water reactors for the last thirty five years. The utilization of such a fuel enables the recycling of plutonium, which is recovered from spent nuclear fuel (Bairiot and Deramaix, 1992; Degueldre et al., 2011a). MOX is burnt in commercial reactors together with conventional uranium dioxide fuel. However, it enables a possible oxidation or reduction of the actinides in the fuel matrix, which could render them more labile in a cladding failure event or in the case of groundwater intrusion in a geological repository. An understanding of the actinide based redox species in the MOX fuel at atomic and multiscale levels is therefore highly relevant.

Since the oxidation state of thorium does not depend on its local environment (there is only one stable oxidation state (IV) in non-extreme conditions (Lide, 2006; Shuller et al., 2011)), its characterization in pristine and irradiated MOX samples can be used as a starting point for the study of other actinides with the same oxidation state. At the Laboratory for Nuclear Materials (LNM), in the Paul Scherrer Institut (PSI), research has been focused on homogeneous fuel production, such as MOX or inert matrix fuel fabrication by the internal gelation technique (Ledergerber, 1982; Pouchon et al., 2003); continuing efforts are being made to further simplify the process (Cozzo et al., 2012). This fabrication route offers a production of the material with a randomized atomic environment at the beginning of irradiation in the reactor. This simplifies the study of the microstructural development in MOX fuel, and/or the element-specific next-neighbor atomic environment in as-prepared as well as in irradiated MOX fuel. The latter has been investigated by spatially resolved X-ray absorption fine structure (XAFS) spectroscopy, a technique used to gain information on element-specific nearest-neighbor atomic environment (Degueldre et al., 2010; Conradson et al., 2005; Denecke, 2006).

The analyses of the experimental XAFS spectra provide information about the physical and chemical structure of matter at atomic scale (Okamoto, 2004; Teo and Joy, 1981; Wang et al., 2004). Due to significant advances in X-ray absorption spectroscopy in the last years, several measurements on nuclear materials have been published (Conradson et al., 2004; Yamamoto et al., 2008; Nishi et al., 2010; Martin et al., 2007; Degueldre et al., 2013). Simulations of the experiments (Skomurski et al., 2008) and the theoretical studies of fitting parameters can be readily performed on personal computers. In this study the FEFF software (Ankudinov et al., 1998, 2003) is used; it is an ab initio self-consistent real space multiple-scattering code for simultaneous calculations of x-ray absorption spectra and electronic structure. Upon entering simple (e.g. the lattice parameter) or more complex parameter values representing the atomic structure of the sample, it returns a calculated XAFS spectrum, which can be compared with actual XAFS measurements carried out at the Swiss Light Source (SLS) at

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0149-1970/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.pnucene.2013.09.009

the Paul Scherrer Institute (PSI) (Degueldre et al., 2011b). This is possible when the atom positions and species near the absorber are known with reasonable accuracy. The IFEFFIT package (Newville, 2005) is used to analyze the measured spectra. Pristine ThO_2 powder was also measured by XAFS and is used as a reference.

2. Experimental and modeling

2.1. Samples

The MOX sphere-pac fuel analyzed in this study has been fabricated at PSI by internal gelation process (Ingold et al., 2002). The produced MOX sphere-pac fuel segments were irradiated in the Swiss pressurized water reactor (PWR) Beznau-1 of Axpo AG. A burn-up of 60 MW d kg^{-1} of heavy metal was reached after a 6 year irradiation period. The sample was examined in the rim region where the local burn up is about 100 MWd kg^{-1}. Further information concerning the conditions of the spheres fabrication, the preparation of the samples for XAFS measurements as well as a discussion on the results were described earlier (Degueldre et al., 2011b). In a similar way, a pristine sample of the same fuel was also prepared. In order to obtain a reference XAFS spectrum of pure thoria, 1.7 mg powder (ThO_2 Fluka purissima) was laid on a kapton adhesive surface as a 5 μm thick layer. This thickness range was chosen in order to perform simultaneous fluorescence and transmission measurements. EPMA and XRF studies on the MOX sample showed a concentration of thorium about 1590 ppm before irradiation.

2.2. X-ray absorption analysis

The spatially resolved EXAFS investigations were carried out at the micro-XAS beamline of the Swiss Light Source. This is a dedicated hard X-ray microprobe beamline using a fixed-exit Si(111) double-crystal monochromator and covering an energy scale from 4 to 23 keV. The micro-XAS beamline was presented earlier (Borca et al., 2009). A single-element Si-drift detector was used to simultaneously record the fluorescence lines and the transmission from the Th containing samples. All experiments were performed in air and at room temperature. The beam size was 3 μm × 3 μm.

The energy calibration of the monochromator was performed with a Zr reference foil at 17,998 eV.

The peeling test methodology (replicate) was used to extract a specimen from the surface of the irradiated pellet. The circularly polished surface of the fuel section was pressed on a piece of adhesive Kapton tape. The peeled sample was thus formed of microparticles. For radioprotection purposes, the size of the sample needed to be reduced. In a laminar fume hood, the subsampling was performed by cutting an area of the replicate. The peeling and subsampling are described in (Degueldre et al., 2011b).

2.3. Modeling

The Athena (Ravel and Newville, 2005) software was used to normalize, merge and obtain the Fourier Transform of the recorded spectra. The Artemis code was used to fit combinations of calculated spectra with the recorded ones in order to determine the local atoms distribution at selected location of the pellet (Ravel and Newville, 2005; Ravel, 2001). The MOX measured in this study is a homogeneous fuel. Like the plutonium atoms, the thorium atoms are expected (in the pristine fuel) to be randomly distributed as a solid solution within the UO_2 matrix, which has a fluorite structure like ThO_2 (Fig. 1). Modeling a solid solution is relevant because of the homogeneous preparation route and of the low quantity of thorium. As a result, some uranium atoms in the UO_2 matrix are substituted at random positions by plutonium atoms (Martin et al., 2007) or by thorium atoms. The substitution of a uranium atom by a thorium atom is schematically shown in Fig. 1b), where ThO_2 and UO_2 form a solid solution.

Simulations of the structure have been performed with the FEFF code (Ankudinov et al., 1998; Ravel, 2005), where the absorbing atom is located in the center of the modeled supercell. The EXAFS spectra of given crystal structures were calculated and compared to the experimental spectra. In the present work the EXAFS spectra of ThO_2 and $(U,Th)O_2$ were calculated at the L_{III}-edge of thorium and compared with the recorded ones. In the case of a pure crystal, the positions of the atoms are given by the respective ionic radii taken from Shannon (Shannon, 1976). In the case of a solid solution of ThO_2 in UO_2, Hubert (Hubert et al., 2006) has measured the interatomic distances for various Th/U ratios. In our sample the concentration of Th is low, therefore Hubert's values for $(U_{0.91}Th_{0.09})O_2$ are used.

In Hubert's work the Th concentration is much higher than for the MOX currently investigated, however the EXAFS signal is generated by a very large number of atoms. Given the respective concentrations of Th and U in Hubert's sample and the homogeneous preparation route, the metal first neighbor atoms of thorium can be considered to be only uranium. Table 1 reports the interatomic values used in the input file for the FEFF calculation of pure oxides and for mixed oxides. Because of the contraction of the actinide ionic radius (Morss, 1983; Xia and Krupa, 2000) going towards higher atomic numbers, the substitution of an uranium atom by a thorium atom in the UO_2 crystal creates a local distortion of the structure, as illustrated in Fig. 1.

3. Results and discussion

The energy spectra of unirradiated thoria powder and of the irradiated samples are recorded and analyzed. After operating a fast Fourier transform on the recorded and calculated spectra, the results are discussed in order to look into the atomic environment of thorium in irradiated MOX sample.

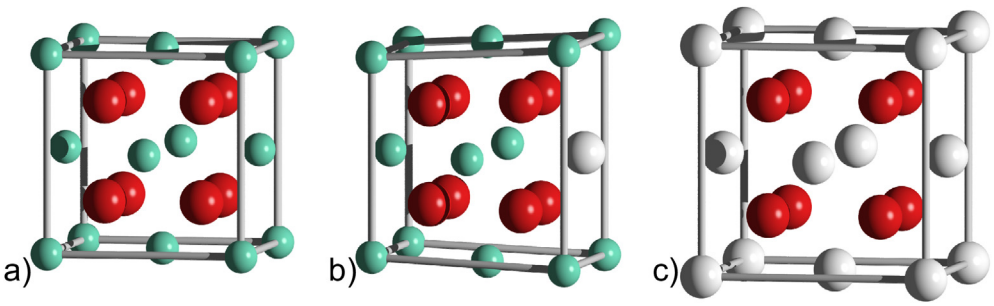

Fig. 1. Schematic view of a *a)* UO_2 and *c)* ThO_2 cell. *b)* The presence of a thorium atom in solid solution with UO_2 creates a distortion in the UO_2 structure. The lattice increase is intentionally magnified (*10) for highlighting purposes. (red = O, green = U, white = Th). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)